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Supporting Information

Diversity-Oriented Enantioselective Synthesis of Highly Functionalized Cyclic and Bicyclic Alcohols

Bin Mao,[a] Martín Fañanás-Mastral,[a] Martin Lutz,[b] and Ben L. Feringa*[a]

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1. General Remarks:

Column chromatography was performed on silica gel (Silica-P flash silica gel from Silicycle, size 40-63 μm). TLC was performed on silica gel 60/Kieselguhr F254. Components were visualized by UV and staining with a solution of a mixture of $KMnO_4$ (10 g) and K_2CO_3 (10 g) in H_2O (500 mL). Mass spectra were recorded on a LTQ Orbitrap XL mass spectrometer (ESI+/APCI+/APPI+) or a Xevo® G2 QTof mass spectrometer with DART ionization. NMR spectra were recorded on a Varian AMX400 (400 and 100.59 MHz, respectively) or a Varian Unity Plus Varian-500 (500 and 125 MHz, respectively) using $CDCl_3$ as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 for ^1H, δ 77.0 for ^{13}C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. Optical rotations were measured in $CHCl_3$ on a *Schmidt + Haensch* polarimeter (Polartronic MH8) with a 10 cm cell (*c* given in g/100 mL). Conversion of the reaction were determined by GC (GC, HP6890: MS HP5973) with an HP5 column (Agilent Technologies, Palo Alto, CA). The regioselectivity of the reaction was determined by by ^1H NMR spectroscopy of the crude mixture. Enantioselectivities were determined by HPLC analysis using a Shimadzu LC-10AD*VP* HPLC equipped with a Shimadzu SPD-M10A*VP* diode array detector.

All reactions were carried out under a nitrogen atmosphere using oven dried glassware and using standard Schlenk techniques. All solvents were reagent grade and were dried and distilled prior to use, if necessary. Tetrahydrofuran and diethylether were distilled over Na/benzophenone. Toluene and dichloromethane were distilled over calcium hydride. All the ligands and $CuBr{\cdot}SMe_2$ were purchased from Aldrich and used without further purification. Alkyl bromides except 4-bromo-1-trimethylsilyl-1-butyne[1] and 5-bromo-1-trimethylsilyl-1-pentyne[1] were purchased from Aldrich. All other commercially available reagents were used as received. Starting material **1a, 1b** and **1c** was synthesized according to the procedure of Trombini and Lombardo et al.[2] Grignard reagents were prepared from the corresponding alkyl bromides and magnesium turnings in Et_2O following standard procedures. Grignard reagents were titrated using *sec*-BuOH and catalytic amounts of 1,10-phenanthroline. Products **3a** and **4a** have been reported in our previous paper.[3]

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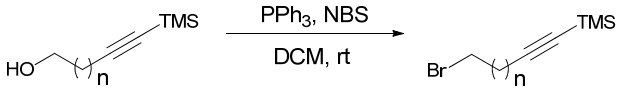
[1] Y. Nishimoto, M. Kajioka, T. Saito, M. Yasuda, A. Baba, *Chem. Commun.* **2008**, 6396-6398.
[2] (a) M. Lombardo, S. Morganti, C. Trombini, *J. Org. Chem.* **2003**, *68*, 997-1006; (b) M. Lombardo, R. Girotti, S. Morganti and C. Trombini, *Chem. Commun.* **2001**, 2310-2311.
[3] K. Geurts, S. P. Fletcher, B. L. Feringa, *J. Am. Chem. Soc.* **2006**, *128*, 15572-15573.

2. Experimental Section

2.1 General preparation of alkyl bromide containing alkyne functional group[1]

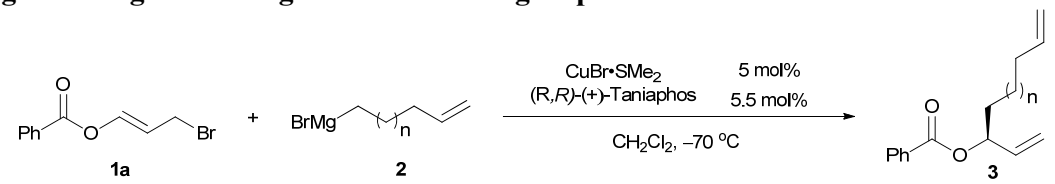


n = 1, 2

TMS = $SiMe_3$

To a solution of PPh_3 (33 mmol, 1.1 equiv) and the particular alcohol (30 mmol) in CH_2Cl_2 (30 mL) at room temperature was added N-bromosuccinimide (32 mmol, 1.07 equiv) and the stirring was continued at room temperature for 5 h. The resulting phosphine oxides were precipitated by washing with the mixture of Pentane/Ether (1:1) and then filtered. The combined solvent was dried over $MgSO_4$ and removed under *vacuo*. The residue was purified by distillation to yield the corresponding alkyl bromide. The physical data were identical in all respects to those previously reported.[1]

2.2 General procedure for copper catalyzed *hetero*-allylic asymmetric alkylation[3] with Grignard reagent bearing terminal alkene group:



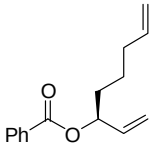
3a n = 1

3b n = 2

3c n = 3

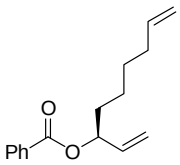
Grignard reagent **2** (0.64 mmol, 2 equiv) in Et_2O was added dropwise over 5 minutes to a homogeneous, stirred and cooled (–70 °C) solution of the allylic bromide (0.32 mmol), CuBr·SMe_2 (5.0 mol%) and (*R,R*)-(+)-Taniaphos (5.5 mol%) in CH_2Cl_2 (3.5 mL) under a nitrogen atmosphere. The reaction mixture was stirred at the indicated temperature (typically overnight) until completion and then quenched with MeOH (5 mL). The reaction mixture was allow to warm to room temperature and sat. aq. NH_4Cl (5 mL) was added. The mixture was partitioned between CH_2Cl_2 (5 mL) and water. The organic layer was dried ($MgSO_4$), filtered and the solvent evaporated under *vacuo*. Purification by flash chromatography over silica gel, using Et_2O/*n*-Pentane (1% to 2%) afforded pure product **3** as colorless oils.

(+)-(*S*)-Octa-1,7-dien-3-yl benzoate (3b)



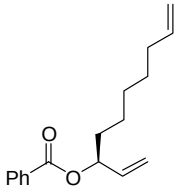
Colorless oil. Yield: 95%. ee: 97%. $[\alpha]_D^{20}$ +33.2 (*c* 3.6 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 6.9 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.99 – 5.68 (m, 2H), 5.62 – 5.44 (m, 1H), 5.33 (d, *J* = 17.2 Hz, 1H), 5.21 (d, *J* = 10.5 Hz, 1H), 5.04 (s, 1H), 5.00 – 4.88 (m, 1H), 2.11 (q, *J* = 7.0 Hz, 2H), 1.90 – 1.67 (m, 2H), 1.52 (dd, *J* = 15.2, 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 138.5, 136.7, 133.1, 130.0, 129.8 (2×*C*), 128.6 (2×*C*), 116.9, 115.1, 75.4, 34.0, 33.7, 24.6. HRMS (ESI+, *m/z*): calcd for $C_{15}H_{18}O_2Na$ $[M+Na]^+$: 253.11990, found 253.12015. Ee was determined by chiral HPLC, Chiralpak OB-H (Heptane/*i*-Propanol = 99/1, 0.5 mL/min, 224 nm, column temperature 40 °C), retention times: t_R (major) 9.94 min, t_R (minor) 11.54 min.

(+)-(*S*)-Nona-1,8-dien-3-yl benzoate (3c)



Colorless oil. Yield: 83%. ee: 96%. $[\alpha]_D^{20}$ +21.4 (*c* 3.4 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.00 (m, 2H), 7.61 – 7.51 (m, 1H), 7.45 (m, 2H), 5.89 (ddd, *J* = 14.4, 10.3, 5.1 Hz, 1H), 5.84 – 5.69 (m, 1H), 5.49 (ddd, *J* = 12.2, 6.1, 1.1 Hz, 1H), 5.38 – 5.28 (m, 1H), 5.20 (dt, *J* = 10.5, 1.2 Hz, 1H), 5.07 – 4.87 (m, 2H), 2.10 – 2.03 (m, 2H), 1.88 – 1.66 (m, 2H), 1.52 – 1.34 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 138.9, 136.8, 133.1, 130.8, 129.8, 128.6, 116.9, 114.7, 75.5, 34.4, 33.8, 28.9, 24.8. HRMS (ESI+, *m/z*): calcd for $C_{16}H_{20}O_2Na$ $[M+Na]^+$: 267.13555, found 267.13507. Ee was determined by chiral HPLC, Chiralpak OB-H (Heptane/*i*-Propanol = 98/2, 0.5 mL/min, 226 nm, column temperature 40°C), retention times: t_R (major) 8.68 min, t_R (minor) 10.00 min.

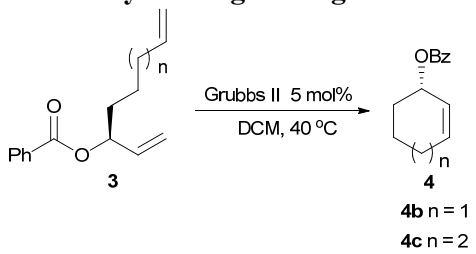
(+)-(*S*)-Deca-1,9-dien-3-yl benzoate (3d)



Colorless oil. Yield: 85%. $[\alpha]_D^{20}$ +26 (*c* 0.6 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.00 (m, 2H), 7.58 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.89 (ddd, *J* = 14.1, 10.2, 4.9 Hz, 1H), 5.84 – 5.73 (m, 1H), 5.50 (dd, *J* = 13.1, 6.2 Hz, 1H), 5.32 (d, *J* = 17.2 Hz, 1H), 5.20 (d, *J* = 10.5 Hz, 1H), 5.05 – 4.89 (m, 2H), 2.04 (dd, *J* = 13.2, 6.4 Hz, 2H), 1.92 – 1.64 (m, 2H), 1.51 – 1.32 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 138.9, 136.6, 132.8, 130.6, 129.6, 128.3, 116.6, 114.3, 75.3, 34.3, 33.6, 28.9, 28.7, 24.9. HRMS (ESI+, *m/z*): calcd for $C_{17}H_{22}O_2Na$

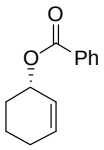
[M+Na]$^+$: 281.15120, found 281.15155. The enantiomeric excess of product could not be determined by chiral GC or HPLC.

2.3 General procedure for Ru-catalyzed ring-closing metathesis (RCM):



Allylic ester **3** (0.6 mmol) was dissolved in degassed CH_2Cl_2 (12 mL) under a N_2 atmosphere. Grubbs 2nd generation catalyst (0.03 mmol) was tipped into the solution and then the mixture was heated under reflux for 18 h (40 °C). The mixture was cooled down to room temperature and the solvents were removed under reduced pressure. Purification by flash chromatography (Ether/*n*-Pentane 1% to 2%) afforded the desired product **4**.

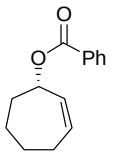
(-)-(*S*)-Cyclohex-2-en-1-yl benzoate (4b)



Colorless oil. Yield: 89%. ee: 95%. $[\alpha]_D^{20}$ -187.3 (*c* 3.7 in $CHCl_3$). [lit.,[4] (*S* isomer, 90% ee): $[\alpha]_D^{20}$ -164 (*c* 0.96 in $CHCl_3$)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 7.83 (m, 2H), 7.61 – 7.50 (m, 1H), 7.48 – 7.34 (m, 2H), 6.11 – 5.94 (m, 1H), 5.90 – 5.80 (m, 1H), 5.51 (dd, *J* = 3.4, 1.6 Hz, 1H), 2.15 – 2.04 (m, 2H), 2.03 – 1.94 (m, 1H), 1.93 – 1.77 (m, 2H), 1.77 – 1.65 (m, 1H). ^{13}C NMR (100 MHz, CDCl3) δ 166.4, 133.1, 133.0, 131.0, 129.8, 128.5, 125.9, 68.8, 28.6, 25.2, 19.2. HRMS (ESI+, *m/z*): calcd for $C_{13}H_{14}O_2Na$ $[M+Na]^+$: 225.08860, found 225.04333. Ee was determined by chiral HPLC, Chiralpak AD-H (Heptane/*i*-Propanol = 99.9/0.1, 0.5 mL/min, 226 nm, column temperature 40°C), retention times: t_R (major) 19.55 min, t_R (minor) 18.66 min.

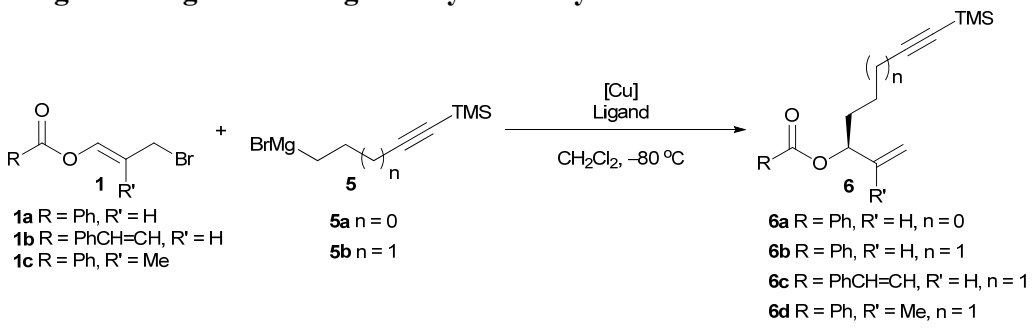
[4] D. R. Boyd, N. D. Sharma, L. Sbircea, D. Murphy, T. Belhocine, J. F. Malone, S. L. James, C. C. R. Allen, J. T. G. Hamilton, *Chem. Comm.* **2008**, 5535-5537.

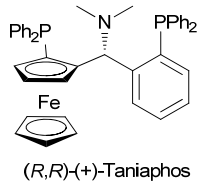
(-)-(*S*)-Cyclohept-2-en-1-yl benzoate (4c)



Colorless oil. Yield: 85%. ee: 95%. $[\alpha]_D^{20}$ -37.4 (*c* 2.3 in $CHCl_3$). [lit.,[4] (*S* isomer, 97% ee): $[\alpha]_D^{20}$ -52 (*c* 0.85 in $CHCl_3$)]. ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.00 (m, 2H), 7.64 – 7.51 (m, 1H), 7.49 – 7.35 (m, 2H), 5.95 – 5.85 (m, 1H), 5.83 – 5.76 (m, 1H), 5.71 – 5.63 (m, 1H), 2.33 – 2.21 (m, 1H), 2.20 – 2.09 (m, 1H), 2.07 – 1.93 (m, 2H), 1.90 – 1.66 (m, 3H), 1.53 – 1.45 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 133.7, 133.0, 132.2, 130.9, 129.8, 128.5, 74.9, 33.1, 28.8, 26.9, 26.8. HRMS (ESI+, *m/z*): calcd for $C_{14}H_{16}O_2Na$ $[M+Na]^+$: 337.12304, found 337.12205. Ee was determined by chiral HPLC, Chiralpak AS-H (Heptane/*i*-Propanol = 99.9/0.1, 0.5 mL/min, 226 nm, column temperature 40°C), retention times: t_R (major) 11.60 min, t_R (minor) 10.50 min.

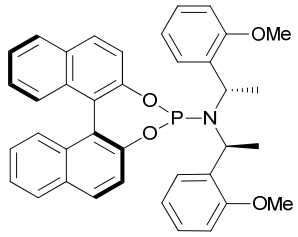
2.4 General procedure for the copper catalyzed *hetero*-allylic asymmetric alkylation with Grignard reagents bearing an alkyne moiety:[3]





(*R*,*R*)-(+)-Taniaphos

L1



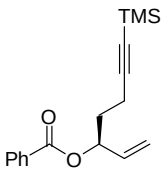
L3

Method A: A solution of the appropriate Grignard reagent **5** (0.48 mmol, 1.5 equiv) in Et_2O (1.5 M and 1.6 M, respectively) was diluted with CH_2Cl_2 (combined volume of 1 mL) and added dropwise for 4h to a homogeneous, stirred and cooled (–80 °C) solution of the allylic bromide (0.32 mmol), CuBr·SMe_2 (5.0 mol%) and **L1** (5.5 mol%) in CH_2Cl_2 (3.2 mL) under a nitrogen atmosphere. The reaction mixture was stirred at that temperature (typically overnight) until completion and quenched with MeOH (5 mL). The mixture was removed from the cooling bath and sat. aq. NH_4Cl (5 mL) was added. The mixture was partitioned

between CH_2Cl_2 and water. The organic layer was dried over $MgSO_4$, filtered and the solvent was evaporated *in vacuo*. Purification by flash chromatography over silica gel, using Et_2O/*n*-Pentane 1% to 2% to afford the products **6a-c** as colorless oils

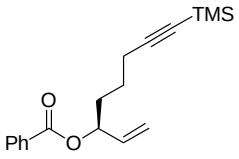
Method B: A solution of the appropriate Grignard reagent **5b** (0.38 mmol, 1.2 equiv) in Et_2O (1.6 M) was diluted with CH_2Cl_2 (combined volume of 1 mL) and added dropwise for 4h to a homogeneous, stirred and cooled (–80 °C) solution of the allylic bromide (0.32 mmol), CuTC (3.0 mol%) and **L3** (3.3 mol%) in CH_2Cl_2 (3.2 mL) under a nitrogen atmosphere. The following steps are the same as described by method A.

(+)-(*S*)-7-(Trimethylsilyl)hept-1-en-6-yn-3-yl benzoate (6a)



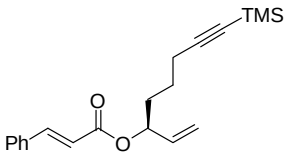
Colorless oil. Yield: 74%. ee: 98%. $[\alpha]_D^{20}$ +14.2 (*c* 1.3 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 9.8, 1.6 Hz, 1H), 7.61 – 7.51 (m, 1H), 7.44 (t, *J* = 6.8 Hz, 1H), 5.98 – 5.79 (m, 1H), 5.57 (dd, *J* = 12.4, 6.6 Hz, 1H), 5.35 (d, *J* = 16.0 Hz, 1H), 5.24 (d, *J* = 10.6 Hz, 1H), 2.36 (t, *J* = 7.5 Hz, 1H), 2.14 – 1.87 (m, 1H), 0.13 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 135.7, 132.9, 130.3, 129.6, 129.6, 128.3, 117.2, 105.9, 85.3, 74.1, 33.3, 16.0, 0.0. HRMS (ESI+, *m/z*): calcd for $C_{17}H_{22}O_2SiNa$ $[M+Na]^+$: 309.12813, found 309.12846. Ee was determined by chiral HPLC, Chiralpak AS-H (Heptane/*i*-Propanol = 99.9/0.1, 0.5 mL/min, 226 nm, column temperature 40°C), retention times: t_R (major) 11.60 min, t_R (minor) 10.50 min.

(+)-(*S*)-8-(Trimethylsilyl)oct-1-en-7-yn-3-yl benzoate (6b)



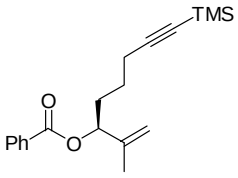
Colorless oil. Yield: 84%. ee: 97%. $[\alpha]_D^{20}$ +10.1 (*c* 5.7 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 7.91 (m, 2H), 7.63 – 7.51 (m, 1H), 7.50 – 7.32 (m, 2H), 6.11 – 5.77 (m, 1H), 5.53 (dd, *J* = 12.7, 6.3 Hz, 1H), 5.34 (d, *J* = 17.2 Hz, 1H), 5.22 (d, *J* = 10.6 Hz, 1H), 2.28 (t, *J* = 7.1 Hz, 2H), 2.01 – 1.81 (m, 2H), 1.75 – 1.54 (m, 2H), 0.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 136.3, 132.9, 130.4, 129.6, 128.3, 116.8, 106.7, 85.0, 74.7, 33.3, 24.2, 19.7, 0.1. HRMS (ESI+, *m/z*): calcd for $C_{18}H_{24}O_2SiNa$ $[M+Na]^+$: 323.14378, found 323.14404. Ee was determined by chiral HPLC, Chiralpak AD-H (Heptane/*i*-Propanol = 99.9/0.1, 0.5 mL/min, 226 nm, column temperature 40 °C), retention times: t_R (major) 13.80 min, t_R (minor) 12.98 min.

(+)-(*S*)-8-(Trimethylsilyl)oct-1-en-7-yn-3-yl cinnamate (6c)



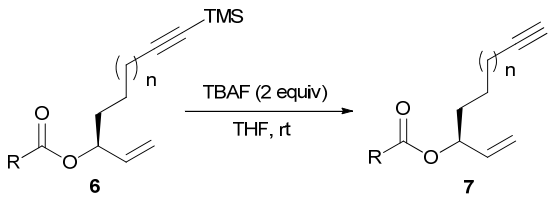
Colorless oil. Yield: 75%. ee: 96%. $[\alpha]_D^{20}$ +16.0 (*c* 0.4 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.60 – 7.47 (m, 2H), 7.44 – 7.29 (m, 3H), 6.46 (d, *J* = 16.0 Hz, 1H), 5.90 – 5.78 (m, 1H), 5.41 (d, *J* = 5.9 Hz, 1H), 5.31 (d, *J* = 15.9 Hz, 1H), 5.21 (d, *J* = 10.5 Hz, 1H), 2.30 – 2.24 (m, 2H), 1.80 (t, *J* = 6.6 Hz, 2H), 1.68 – 1.52 (m, 2H), 0.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 144.8, 136.3, 134.4, 130.3, 128.9, 128.1, 118.3, 116.8, 106.7, 85.0, 74.3, 33.3, 24.2, 19.6, 0.1. HRMS (ESI+, *m/z*): calcd for $C_{20}H_{26}O_2SiNa$ $[M+Na]^+$: 349.15943, found 349.15943. Ee was determined by chiral HPLC, Chiralpak AD-H (Heptane/*i*-Propanol = 99/1, 0.5 mL/min, 270 nm, column temperature 40°C), retention times: t_R (major) 14.48 min, t_R (minor) 12.64 min.

(+)-(*S*)-2-Methyl-8-(trimethylsilyl)oct-1-en-7-yn-3-yl benzoate (6d)



Colorless oil. Yield: 72%. ee: 92%. $[\alpha]_D^{20}$ +13.0 (*c* 1.9 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.64 – 7.52 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.44 (t, *J* = 6.5 Hz, 1H), 5.05 (s, 1H), 4.94 (s, 1H), 2.28 (t, *J* = 6.9 Hz, 2H), 1.91 (dt, *J* = 14.4, 4.7 Hz, 2H), 1.81 (s, 3H), 1.70 – 1.52 (m, 2H), 0.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) 165.71, 142.9, 132.9, 130.5, 129.6, 128.3, 112.8, 106.7, 85.1, 77.3, 31.7, 24.3, 19.6, 18.2, 0.1. HRMS (APCI+, *m/z*): calcd for $C_{19}H_{27}O_2Si$ $[M+H]^+$: 315.17748, found 315.17749. Ee was determined by chiral HPLC, Chiralpak AD-H (Heptane/*i*-Propanol = 99.9/0.1, 0.5 mL/min, 226 nm, column temperature 40°C), retention times: t_R (major) 14.62 min, t_R (minor) 12.83 min.

2.5 General procedure for deprotection of trimethylsilyl (TMS) alkynes

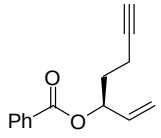


7a R = Ph, n = 0
7b R = Ph, n = 1
7c R = PhCH=CH, n = 1

In a roundbottom flask, a solution of tetra-*n*-butylammonium fluoride (TBAF) (1.0M in THF) (2.0 equiv) was added dropwise to a solution of allylic ester **6** (1.0 equiv) in dry THF

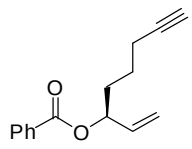
(0.05 M) at 0 °C. The mixture was allowed to warm to rt over 1h. The reaction was quenched with water and extracted with ether (3×). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated. The crude material was purified by column chromatography over silica gel (Et_2O/*n*-Pentane 1% to 2%) to yield the desired product **7**.

(+)-(*S*)-Hept-1-en-6-yn-3-yl benzoate (7a)



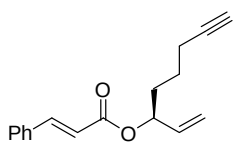
Colorless oil. Yield: 74%. ee: 98%. $[\alpha]_D^{20}$ +15.6 (*c* 0.8 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 – 7.99 (m, 2H), 7.59 – 7.54 (m, 1H), 7.46 – 7.43 (m, 2H), 6.01 – 5.80 (m, 1H), 5.61 (dd, *J* = 12.9, 6.3 Hz, 1H), 5.37 (d, *J* = 17.2 Hz, 1H), 5.25 (d, *J* = 10.6 Hz, 1H), 2.33 (td, *J* = 7.3, 2.6 Hz, 2H), 2.19 – 1.85 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 135.6, 133.0, 130.3, 129.6, 128.4, 117.3, 83.1, 73.9, 69.0, 33.1, 14.6. HRMS (ESI+, *m/z*): calcd for $C_{14}H_{14}O_2Na$ $[M+Na]^+$: 237.08860, found 237.08813. Ee was determined by chiral HPLC, Chiralpak AD-H (Heptane/*i*-Propanol = 99/1, 0.5 mL/min, 226 nm, column temperature 40°C), retention times: t_R (major) 17.15 min, t_R (minor) 14.71 min.

(+)-(*S*)-Oct-1-en-7-yn-3-yl benzoate (7b)



Colorless oil. Yield: 85%. ee: 97%. $[\alpha]_D^{20}$ +18.7 (*c* 3.7 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 – 7.97 (m, 2H), 7.63 – 7.51 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.90 (ddd, *J* = 16.9, 10.5, 6.2 Hz, 1H), 5.55 (d, *J* = 6.2 Hz, 1H), 5.34 (d, *J* = 17.2 Hz, 1H), 5.22 (d, *J* = 10.5 Hz, 1H), 2.25 (m, 2H), 1.97 (s, 1H), 1.89 (m, 2H), 1.78 – 1.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 136.2, 132.9, 130.4, 129.6, 128.3, 116.9, 83.8, 74.7, 68.8, 33.3, 24.0, 18.2. HRMS (ESI+, *m/z*): calcd for $C_{15}H_{16}O_2Na$ $[M+Na]^+$: 251.10425, found 251.10459. Ee was determined by chiral HPLC, Chiralpak OB-H (Heptane/*i*-Propanol = 98/2, 0.5 mL/min, 226 nm, column temperature 40 °C), retention times: t_R (major) 13.95 min, t_R (minor) 16.48 min.

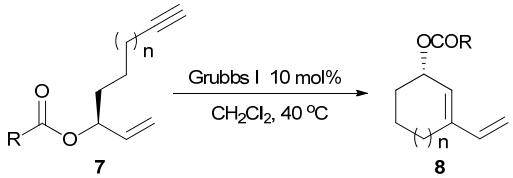
(+)-(*S*)-Oct-1-en-7-yn-3-yl cinnamate (7c)



Colorless oil. Yield: 83%. ee: 96%. $[\alpha]_D^{20}$ +33 (*c* 1.1 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.60 – 7.48 (m, 2H), 7.45 – 7.36 (m, 3H), 6.46 (d, *J* = 16.0 Hz, 1H), 5.85 (ddd, *J* = 17.0, 10.5, 6.3 Hz, 1H), 5.41 (dd, *J* = 13.0, 6.2 Hz, 1H), 5.31 (dt, *J* = 17.2, 1.3 Hz, 1H), 5.21 (dt, *J* = 10.5, 1.2 Hz, 1H), 2.25 (td, *J* = 7.0, 2.6 Hz, 2H), 1.97 (s, 1H), 1.88 – 1.78 (m, 2H),

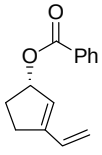
1.70 – 1.57 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 144.9, 136.3, 134.4, 130.3, 128.9, 128.1, 118.2, 116.9, 83.9, 74.3, 68.7, 33.2, 24.0, 18.2. HRMS (ESI+, *m/z*): calcd for $C_{17}H_{18}O_2Na$ $[M+Na]^+$: 277.11990, found 277.12027. Ee was determined by chiral HPLC, Chiralpak OJ-H (Heptane/*i*-Propanol = 99/1, 0.5 mL/min, 270 nm, column temperature 40 °C), retention times: t_R (major) 31.19 min, t_R (minor) 35.12 min.

2.6 General procedure for the Ru-catalyzed ene-yne metathesis:[5]



The corresponding substrate **7a-c** was dissolved in degassed CH_2Cl_2 (0.05 M) and Grubbs 1st generation catalyst (10 mol%) was added to the solution in two portions. The mixture was refluxed under an ethylene atmosphere (1 atm, balloon) until full conversion was reached (24-48h), as indicated by TLC. The mixture was concentrated after filtration through a pad of silica and purified by column chromatography over silica gel (Et_2O/*n*-Pentane 1% to 2%) to yield the desired products **8a-c** as colourless oils.

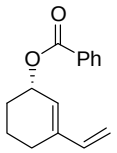
(-)-(*S*)-3-Vinylcyclopent-2-en-1-yl benzoate (8a)



Colorless oil. Yield: 43%. ee: 98%. $[\alpha]_D^{20}$ -145.4 (*c* 3.2 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.95 (m, 2H), 7.53 (dd, *J* = 10.5, 4.3 Hz, 1H), 7.39-7.46 (m, 2H), 6.62 (dd, *J* = 17.5, 10.6 Hz, 1H), 6.04 – 5.93 (m, 1H), 5.88 (s, 1H), 5.29 (d, *J* = 17.5 Hz, 1H), 5.25 (d, *J* = 10.7 Hz, 1H), 2.76 – 2.65 (m, 1H), 2.41-2.55 (m, 2H), 2.07 (ddd, *J* = 8.7, 6.4, 3.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 148.2, 132.8, 132.7, 130.7, 129.6, 128.2, 127.8, 117.5, 81.0, 30.1, 29.2. TOF-MS (DART, *m/z*): calcd for $C_{14}H_{14}O_2$ $[M+H]^+$: 215.1028, found 215.0989. Ee was determined by chiral HPLC, Chiralpak OB-H (Heptane/*i*-Propanol = 99/1, 0.5 mL/min, 226 nm, column temperature 40 °C), retention times: t_R (major) 17.73 min, t_R (minor) 11.67 min.

[5] J. F. Teichert, S. Zhang, A. W. van Zijl, J. W. Slaa, A. J. Minnaard, B. L. Feringa, *Org. Lett.* **2010**, *12*, 4658-4660.

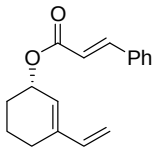
(-)-(*S*)-3-Vinylcyclohex-2-en-1-yl benzoate (8b)



Colorless oil. Yield: 87%. ee: 96%. $[\alpha]_D^{20}$ -204 (*c* 5.5 in $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.02 (m, 2H), 7.64 – 7.50 (m, 1H), 7.49 – 7.28 (m, 2H), 6.38 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.86 (d, *J* = 3.5 Hz, 1H), 5.62 (d, *J* = 4.3 Hz, 1H), 5.27 (d, *J* = 17.5 Hz, 1H), 5.09 (d, *J* = 10.8 Hz, 1H), 2.30 (dt, *J* = 17.3, 5.7 Hz, 1H), 2.23 – 2.09 (m, 1H), 2.06 – 1.83 (m, 3H), 1.83 – 1.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 140.7, 139.0, 132.8, 130.7, 130.5, 129.6, 128.3, 126.4, 113.5, 69.5, 28.4, 23.6, 19.1. HRMS (ESI+, *m/z*): calcd for $C_{15}H_{16}O_2Na$ $[M+Na]^+$: 251.10425, found 251.10461. Ee was determined by chiral HPLC, Chiralpak OB-H (Heptane/*i*-Propanol = 99/1, 0.5 mL/min, 226 nm, column temperature 40 °C), retention times: t_R (major) 15.08 min, t_R (minor) 10.45 min.

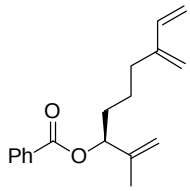
(-)-(*S*)-3-Vinylcyclohex-2-en-1-yl benzoate (8c)



Colorless oil. Yield: 85%. ee: 96%. $[\alpha]_D^{20}$ -197 (*c* 3.1 in $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 16.0 Hz, 1H), 7.55 (dd, *J* = 6.7, 2.8 Hz, 2H), 7.44 – 7.37 (m, 3H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.41 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.83 (d, *J* = 3.3 Hz, 1H), 5.54 (d, *J* = 4.0 Hz, 1H), 5.29 (d, *J* = 17.4 Hz, 1H), 5.12 (d, *J* = 10.8 Hz, 1H), 2.31 (dt, *J* = 17.2, 5.6 Hz, 1H), 2.23 – 2.14 (m, 1H), 2.03 – 1.70 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 147.3, 143.4, 141.7, 137.2, 132.9, 131.6, 130.7, 129.1, 121.2, 116.2, 71.6, 31.2, 26.4, 21.5. HRMS (ESI+, *m/z*): calcd for $C_{17}H_{18}O_2Na$ $[M+Na]^+$: 277.11990, found 277.12029. Ee was determined by chiral HPLC, Chiralpak AS-H (Heptane/*i*-Propanol = 99/1, 0.5 mL/min, 221 nm, column temperature 40°C), retention times: t_R (major) 10.54 min, t_R (minor) 14.00 min.

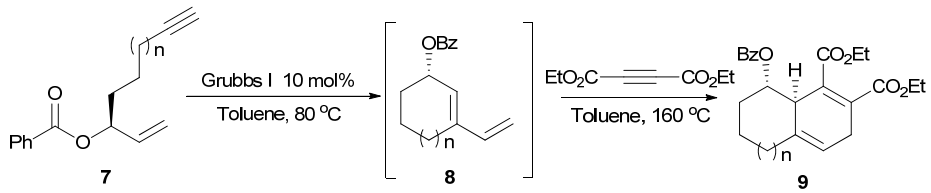
(+)-(*S*)-2-Methyl-7-methylenenona-1,8-dien-3-yl benzoate (8d)



In a roundbottom flask, a solution of tetra-*n*-butylammonium fluoride (TBAF) (1.0M in THF) (2.0 equiv) was added dropwise to a solution of allylic ester **6d** (1.0 equiv) in dry THF (0.05 M) at 0 °C. The mixture was allowed to warm to rt over 1h. The reaction was quenched with water and extracted with ether (3×10 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated. The corresponding intermediate **7d** was then dissolved in degassed CH_2Cl_2 (0.05 M) and Grubbs 1st

generation catalyst (10 mol%) was added to the solution in two portions. The mixture was refluxed under an ethylene atmosphere (1 atm, balloon) until full conversion was reached (20h), as indicated by GC-MS. The mixture was concentrated after filtration through a pad of silica and purified by column chromatography over silica gel (Et_2O/*n*-Pentane 1% to 2%) to yield the desired products **8d** as colourless oil in 66% yield. $[\alpha]_D^{20}$ +11 (*c* 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 – 7.88 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.68 (d, *J* = 2.9 Hz, 1H), 5.42 (d, *J* = 6.5 Hz, 1H), 5.39 (d, *J* = 3.0 Hz, 1H), 5.03 (s, 1H), 4.92 (s, 1H), 4.83 (s, 1H), 4.81 (s, 1H), 2.24 (t, *J* = 7.4 Hz, 2H), 1.79 (s, 3H), 1.77 – 1.66 (m, 2H), 1.57 – 1.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 152.9, 151.2, 143.2, 132.8, 130.6, 129.6, 128.3, 125.3, 112.7, 111.5, 77.8, 35.2, 32.3, 23.6, 18.2. HRMS (APCI+, *m/z*): calcd for $C_{18}H_{23}O_2$ $[M+H]^+$: 271.16926, found 271.16884.

2.7 General procedure for one-pot consecutive Enyne metathesis /Diels−Alder reaction:



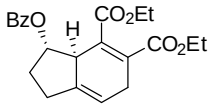
7
7a n= 0
7b n =1

8

9
9a n= 0
9b n =1

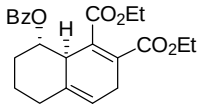
Substrate (**7a-b**) was dissolved in dry toluene (0.05 M) and Grubbs 1st generation catalyst (10 mol%) was added to the solution in two portions (5 mol% at the beginning and 5 mol% after 6 h). The mixture was refluxed in toluene (80 ^{o}C) under an ethylene atmosphere (1 atm, balloon) until full conversion to dienol ester (**8a-b**) was reached, as indicated by TLC. Then diethyl acetylenedicarboxylate (10 equiv) was added dropwise and the resulting solution was heated at 160 ^{o}C in a sealed tube until TLC analysis indicated complete consumption of diene (**8a-b**). The reaction mixture was filtered through a plug of Silica and concentrated *in vacuo*. The residue was subjected to flash chromatography over silica gel (EtOAc/*n*-Pentane 10% to 20%) to yield the desired products (**9a-b**). The stereochemical outcome was determined by ^{1}H-NMR and NOESY analysis.

(+)-(3*S*,3a*R*)-Diethyl 3-(benzoyloxy)-2,3,3a,6-tetrahydro-1*H*-indene-4,5-dicarboxylate (9a)



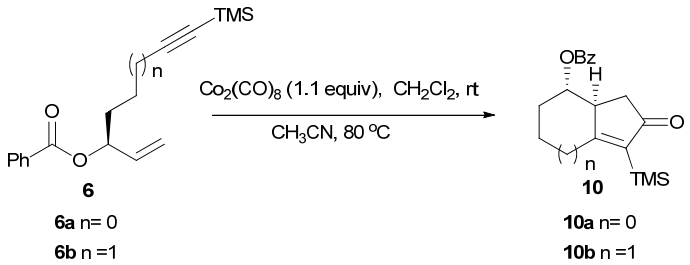
Colorless oil. Yield: 54%. ee: 97%. $[\alpha]_D^{20}$ +70.2 (*c* 0.7 in $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 5.62 (s, 1H), 5.22 (dd, *J* = 16.5, 7.5 Hz, 1H), 4.19 – 4.24 (m, 4H), 3.96 – 4.01 (m, 1H), 3.83 – 3.89 (m, 1H), 3.62 (d, *J* = 9.2 Hz, 1H), 3.19 (dt, *J* = 22.6, 6.0 Hz, 1H), 2.99 (dd, *J* = 22.5, 11.9 Hz, 1H), 2.58 (d, *J* = 11.8 Hz, 1H), 2.39 – 2.48 (m, 2H), 1.85 – 1.74 (m, 1H), 1.29 (t, *J* = 7.3 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 168.5, 168.4, 141.8, 138.1, 135.8, 132.6, 132.3, 131.1, 130.5, 119.1, 64.0, 63.8, 48.9, 32.4, 32.3, 30.6, 29.5, 16.7, 16.3. HRMS (ESI+, *m/z*): calcd for $C_{22}H_{25}O_6$ $[M+H]^+$: 385.16456, found 385.16560. Ee was determined by chiral HPLC, Chiralpak OJ-H (Heptane/*i*-Propanol = 97/3, 0.5 mL/min, 232 nm, column temperature 40 °C), retention times: t_R (major) 10.54 min, t_R (minor) 14.00 min.

(+)-(8*S*,8a*R*)-Diethyl 8-(benzoyloxy)-3,5,6,7,8,8a-hexahydronaphthalene-1,2 dicarboxylate (9b)



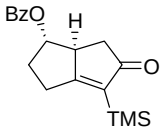
Colorless oil. Yield: 68%. ee: 96%. $[\alpha]_D^{20}$ +87 (*c* 2.4 in $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.57 (dd, *J* = 10.6, 4.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 5.58 (s, 1H), 4.90 (td, *J* = 10.7, 4.4 Hz, 1H), 4.20 (dq, *J* = 10.9, 7.1 Hz, 1H), 4.11 (dq, *J* = 10.9, 7.1 Hz, 1H), 3.80 (dq, *J* = 10.7, 7.2 Hz, 1H), 3.64 (dt, *J* = 11.2, 6.7 Hz, 1H), 3.45 (dq, *J* = 10.7, 7.2 Hz, 1H), 3.18 (dd, *J* = 23.2, 7.3 Hz, 1H), 2.85 (dddd, *J* = 23.2, 6.1, 3.9, 2.3 Hz, 1H), 2.34 (d, *J* = 13.0 Hz, 1H), 2.27 (dd, *J* = 12.5, 3.4 Hz, 1H), 2.02 (t, *J* = 13.0 Hz, 1H), 1.91 (d, *J* = 13.1 Hz, 1H), 1.71 – 1.59 (m, 1H), 1.54 – 1.42 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.78 (t, *J* = 7.2 Hz, 3H). Apt NMR (125 MHz, $CDCl_3$) δ 169.4, 167.3, 165.5, 135.0, 134.6, 133.2, 131.7, 130.2, 129.9, 128.4, 117.5, 77.1, 61.3, 61.2, 45.0, 34.7, 32.9, 28.0, 25.1, 14.2, 13.2. HRMS (ESI+, *m/z*): calcd for $C_{23}H_{29}O_6Na$ $[M+Na]^+$: 421.16216, found 421.16245. Ee was determined by chiral HPLC, Chiralpak OJ-H (Heptane/*i*-Propanol = 99/1, 0.5 mL/min, 233 nm, column temperature 40 °C), retention times: t_R (major) 32.440 min, t_R (minor) 28.68 min.

2.8 General procedure for the Pauson-Khand reaction:[6]



A solution of enyne **6** (1.0 equiv) in dry CH_2Cl_2 (0.05 M) was added to a flask containing $Co_2(CO)_8$ (1.1 equiv) under a N_2 atmosphere. The resulting solution was stirred at RT for 2h until TLC analysis showed that formation of the cobalt complex was complete, and the solvent was then removed *in vacuo*. The residue was diluted with CH_3CN (0.025 M) and the resulting solution was heated to 80 °C until disappearance of the cobalt complex (purple). The reaction mixture was filtered through a plug of Silica and washed by diethyl ether. The combined organic solvents were evaporated and the residue was purified by chromatography over silica gel (EtOAc/*n*-Pentane 5% to 20%) to yield the desired products **10**.

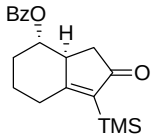
(-)-(1*S*,6a*S*)-5-Oxo-4-(trimethylsilyl)-1,2,3,5,6,6a-hexahydropentalen-1-yl benzoate (10a)



Colorless crystalls. Yield: 64%. ee: 98%. $[\alpha]_D^{20}$ -19 (*c* 0.8 in $CHCl_3$). M.p. 85-91 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.4 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 4.99 (dd, *J* = 17.3, 8.9 Hz, 1H), 3.32 – 3.18 (m, 1H), 2.94 (ddd, *J* = 18.4, 11.7, 2.5 Hz, 1H), 2.82 – 2.71 (m, 1H), 2.67 (dd, *J* = 17.9, 6.6 Hz, 1H), 2.64 – 2.57 (m, 1H), 2.42 (dd, *J* = 17.8, 3.9 Hz, 1H), 2.21 (tt, *J* = 12.7, 8.4 Hz, 1H), 0.24 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 215.9, 193.9, 169.1, 141.2, 135.8, 132.6, 132.3, 131.1, 55.3, 44.7, 34.3, 29.3, 1.5. HRMS (ESI+, *m/z*): calcd for $C_{18}H_{22}O_3SiNa$ $[M+Na]^+$: 337.12304, found 337.12205. Ee was determined by chiral HPLC, Chiralpak AS-H (Heptane/*i*-Propanol = 99/1, 0.5 mL/min, 229 nm, column temperature 40 °C), retention times: t_R (major) 12.56 min, t_R (minor) 11.75 min.

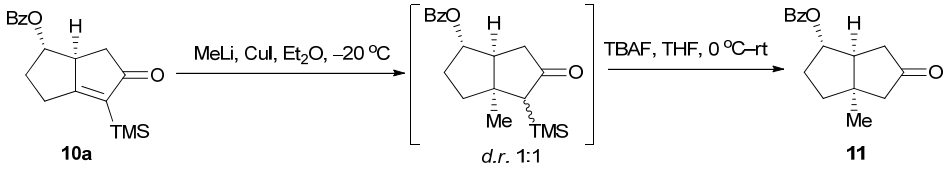
[6] a) J. Adrio, M. R. Rivero, J. C. Carretero, *Chem. -Eur. J.* **2001**, *7*, 2435-2448; b) R. A. Bauer, C. M. Diblasi, D. S. Tan, *Org. Lett.* **2010**, *12*, 2084-2087.

(+)-(7*S*,7a*S*)-2-Oxo-3-(trimethylsilyl)-2,4,5,6,7,7a-hexahydro-1*H*-inden-7-yl benzoate (10b)



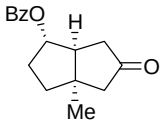
Colorless crystalls. Yield: 55%. ee: 97%. $[\alpha]_D^{20}$ +166.2 (*c* 1.0 in $CHCl_3$). M.p. 79-82 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.0, 0.9 Hz, 2H), 7.60 (dd, *J* = 10.5, 4.3 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 4.78 (td, *J* = 10.9, 4.3 Hz, 1H), 3.06 (d, *J* = 13.8 Hz, 1H), 3.02 – 2.93 (m, 1H), 2.54 (dd, *J* = 18.7, 6.9 Hz, 1H), 2.37 – 2.30 (m, 1H), 2.30 – 2.17 (m, 1H), 2.16 – 2.07 (m, 1H), 1.85 – 1.64 (m, 1H), 1.65 – 1.47 (m, 1H), 0.34 – 0.02 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.7, 185.5, 165.9, 139.5, 133.1, 130.2, 129.6, 128.4, 78.5, 49.0, 40.1, 31.2, 30.3, 23.8, -0.4. HRMS (ESI+, *m/z*): calcd for $C_{19}H_{24}O_3SiNa$ $[M+Na]^+$: 351.13869, found 351.13911. Ee was determined by chiral HPLC, Chiralpak AD-H (Heptane/*i*-Propanol = 95/5, 0.5 mL/min, 228 nm, column temperature 40 °C), retention times: t_R (major) 14.14 min, t_R (minor) 11.34 min.

2.9 The synthesis of an all-carbon quaternary stereogenic center:



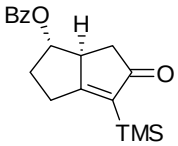
A solution of methyllithium (1.6 M) in dry diethyl ether (0.62 mL, 1 mmol) was slowly added to a suspension of CuI (95.2 mg, 0.5 mmol) in Et_2O (1 mL) at 0 °C under a N_2 atmosphere. The resulting mixture was cooled to -20 ºC before a solution of substrate **10a** (15.7 mg, 0.05 mmol) in ether (1 mL) was added dropwise. After stirring at -20 ºC over 4h, the reaction mixture was quenched with sat. aq. NH_4Cl (4 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (3×5 mL). The combined organic layers were concentrated. After the crude mixture was dissolved in dry THF, tetra-*n*-butylammonium fluoride (TBAF) in THF (0.1 mL, 0.1 mmol) was added dropwise to the solution at ºC. The mixture was allowed to warm to rt over 1h. The organic solvent was removed under *vacuo*. The crude material was purified by column chromatography over silica gel (Et_2O/*n*-Pentane 10% to 20%) to produce the desired product **11** as colorless oil in 62% yield.

(+)-(1*S*,3a*R*,6a*S*)-3a-Methyl-5-oxooctahydropentalen-1-yl benzoate (11)

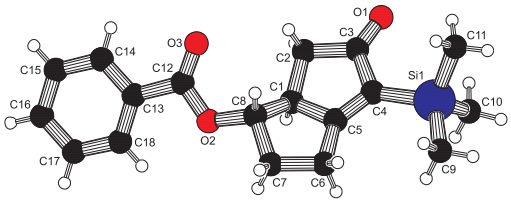


$[\alpha]_D^{20}$ +23.8 (*c* 0.7 in $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.9 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 5.19 (dt, *J* = 6.2, 3.1 Hz, 1H), 2.75 (ddd, *J* = 11.4, 10.4, 1.6 Hz, 1H), 2.56 – 2.46 (m, 1H), 2.42 – 2.21 (m, 4H), 2.13 – 2.03 (m, 1H), 1.97 (dt, *J* = 13.3, 8.0 Hz, 1H), 1.80 (ddd, *J* = 13.5, 8.0, 5.7 Hz, 1H), 1.39 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 220.9, 168.8, 135.5, 133.0, 132.0, 131.0, 85.6, 55.8, 54.8, 48.7, 45.2, 40.9, 34.1, 31.1. HRMS (APPI+, *m/z*): calcd for $C_{16}H_{18}O_3$ $[M+H]^+$: 259.13287, found 259.13288.

3. Crystal structure determination of 10a



10a



Crystal data. $C_{18}H_{22}O_3Si$, Fw = 314.45, colourless plate, 0.52 x 0.44 x 0.04 mm^3, orthorhombic, $P2_12_12_1$ (no. 19), a = 8.6212(3), b = 12.3575(3), c = 15.7882(4) Å, V = 1682.01(8) $Å^3$, Z = 4, D_x = 1.242 g/cm^3, μ = 0.15 mm^{-1}. 31746 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 $Å^{-1}$ at a temperature of 150(2) K. Intensity data were integrated with the Eval15 software.[7] Absorption correction and scaling was performed based on multiple measured reflections with SADABS [8] (0.53-0.75 correction range). 3867 Reflections were unique (R_{int} = 0.028), of which 3660 were observed [I>2σ(I)]. The structure was solved with Direct Methods using the program SHELXS-97[9] and refined with SHELXL-97[9] against F^2 of all reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located in difference Fourier maps and refined with a riding model. 203 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0253 / 0.0665. R1/wR2 [all refl.]: 0.0280 / 0.0677. S = 1.063. Flack parameter[10] x = 0.01(8). Residual electron density between -0.22

[7] A. M. M. Schreurs, X. Xian, L. M. J. Kroon-Batenburg, *J. Appl. Cryst.* **2010**, *43*, 70-82.
[8] *SADABS: Area-Detector Absorption Correction*, v2.10, G. M. Sheldrick, Universität Göttingen, Germany, **1999**.
[9] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.
[10] H. D. Flack, *Acta Cryst.* **1983**, *A39*, 876-881.

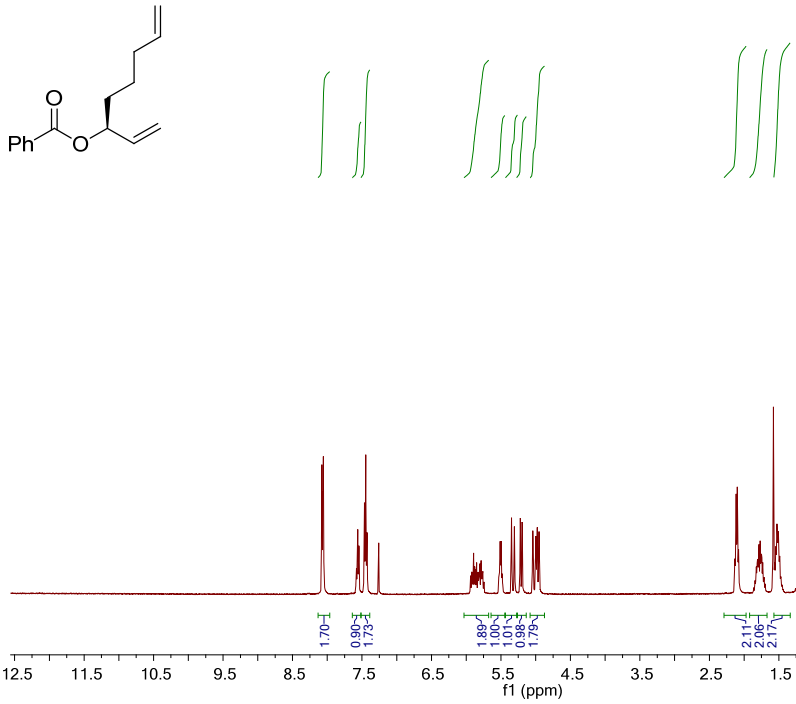
and 0.25 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program[11].

[11] A. L. Spek, *Acta Cryst.* **2009**, *D65*, 148-155.

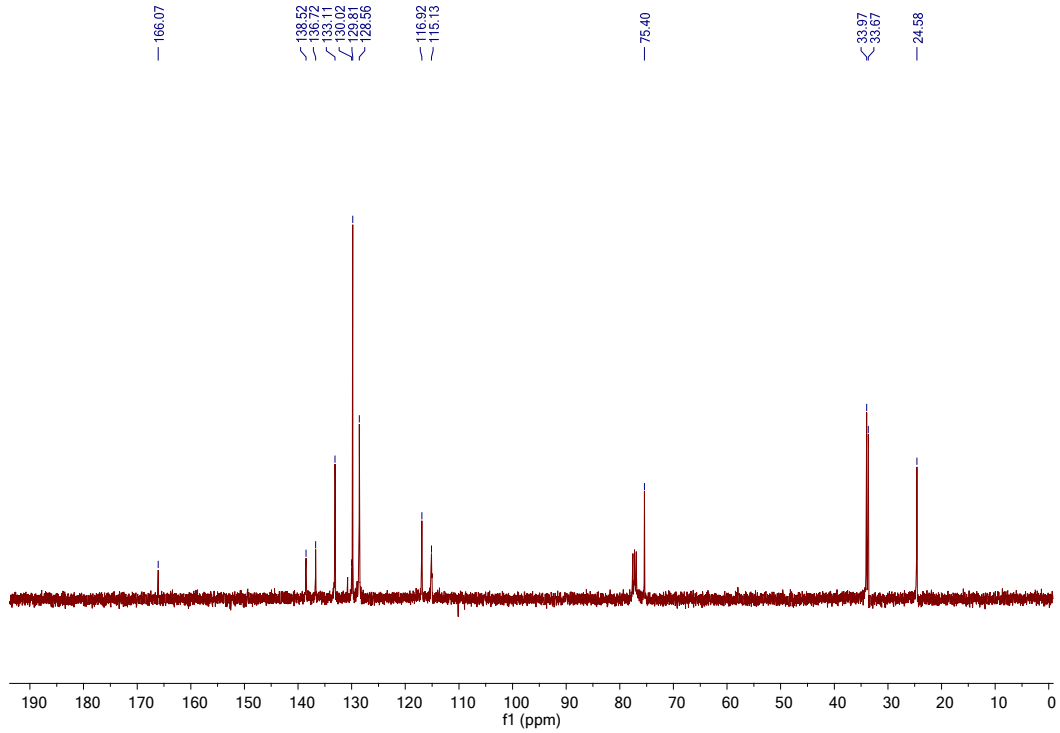
4. NMR Spectroscopy

(+)-(*S*)-Octa-1,7-dien-3-yl benzoate (3a)

^{1}H-NMR

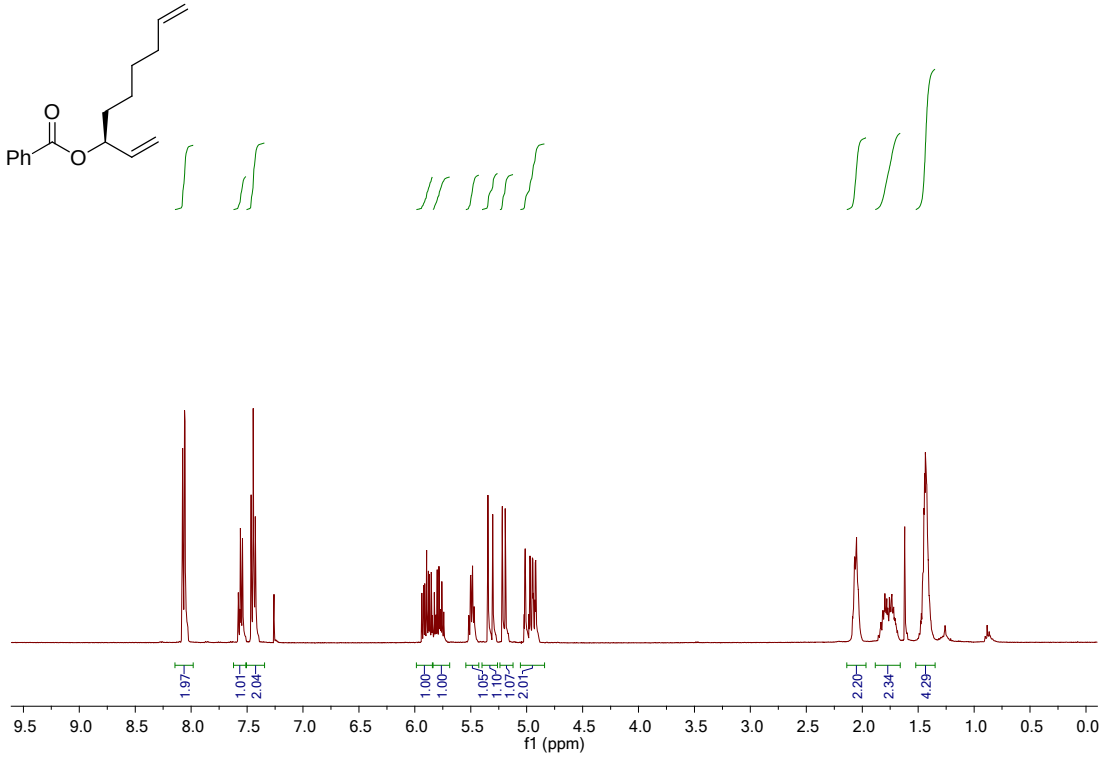


^{13}C-NMR

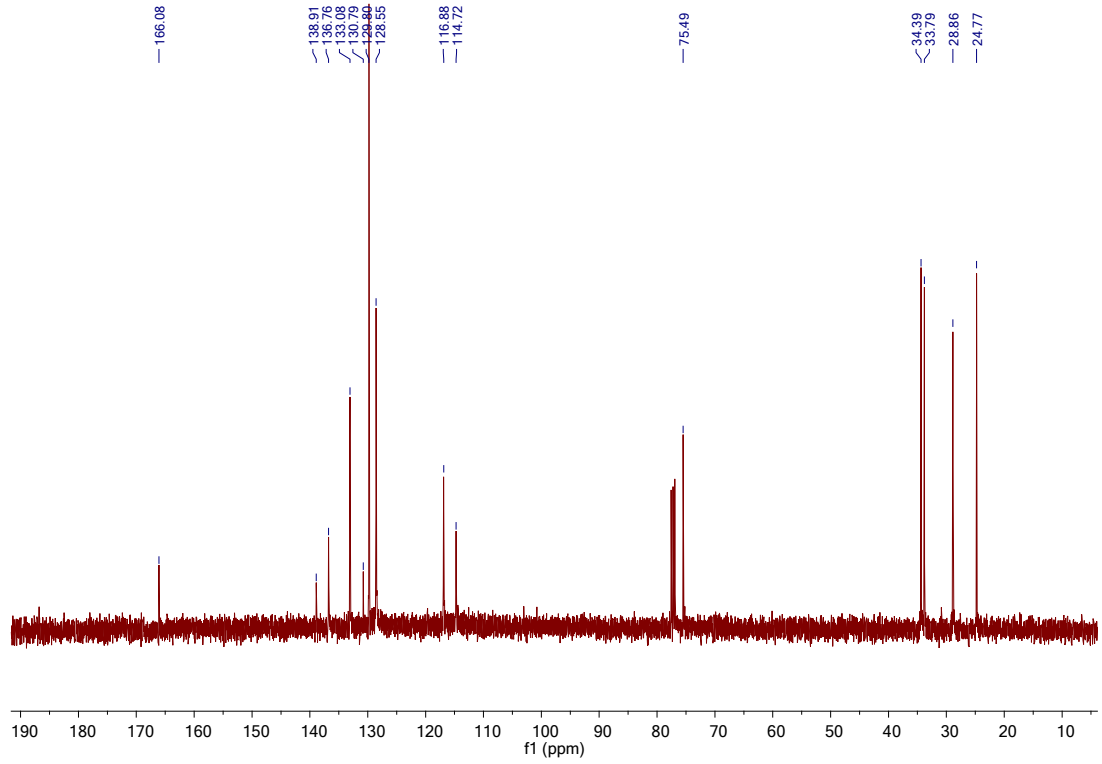


(+)-(*S*)-Nona-1,8-dien-3-yl benzoate (3b)

^{1}H-NMR

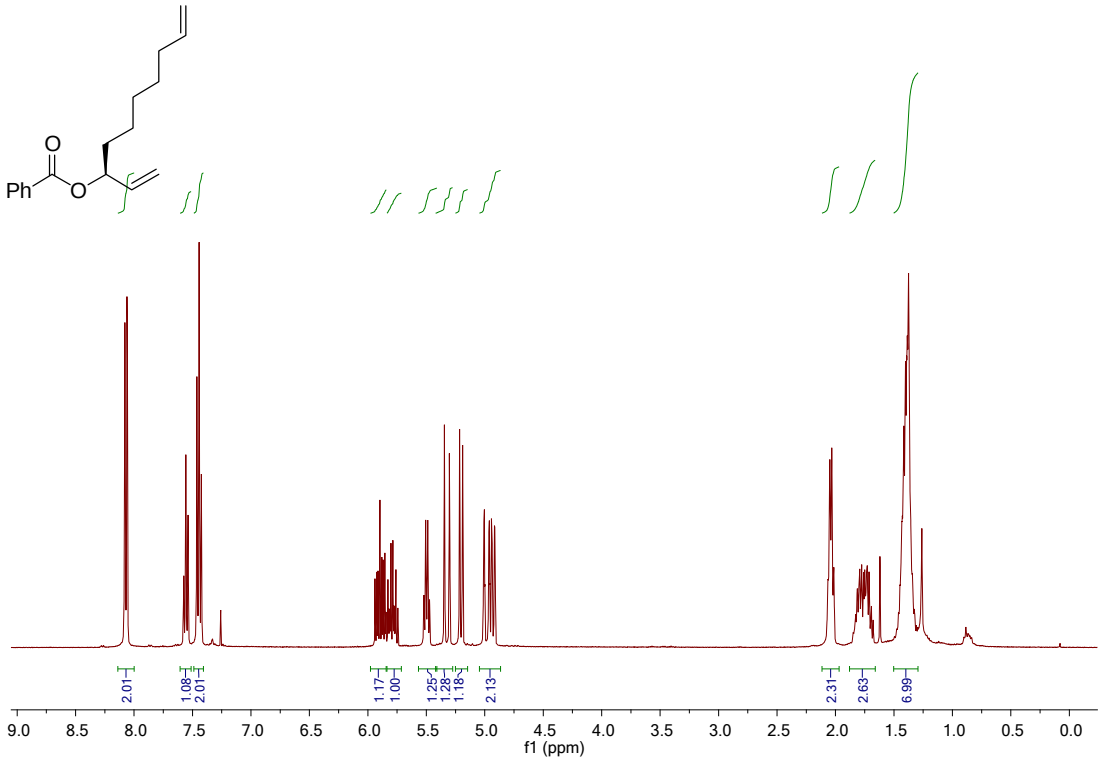


^{13}C-NMR

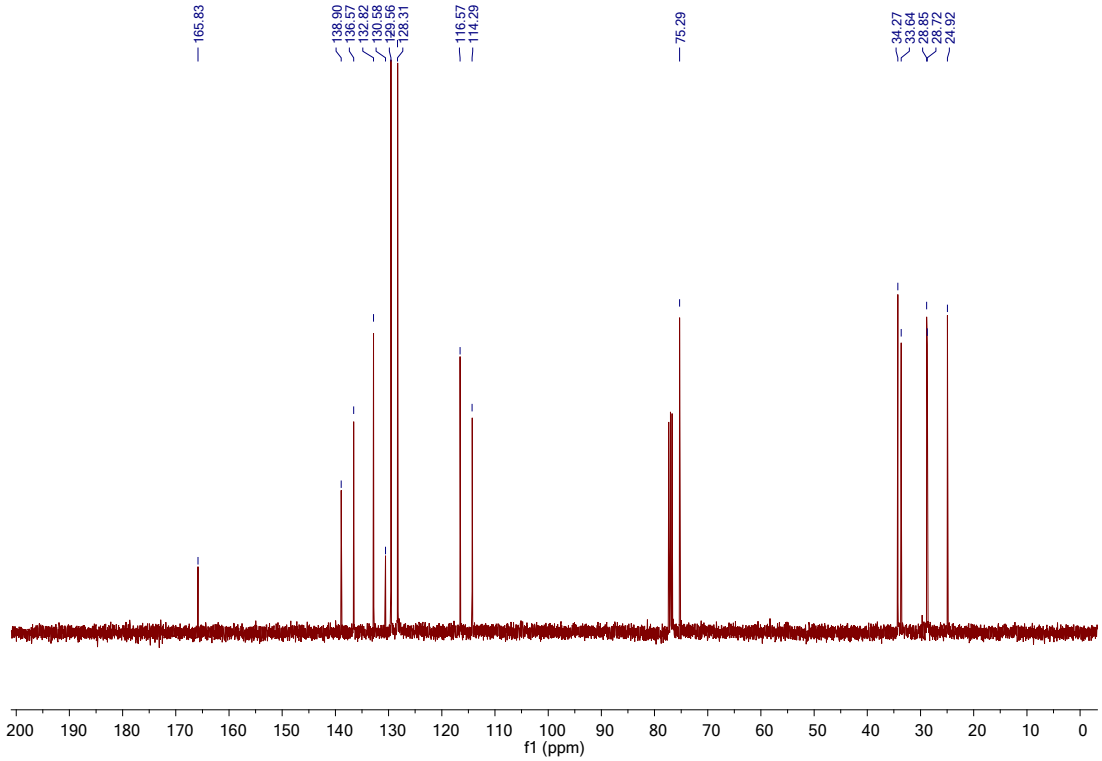


(+)-(*S*)-Deca-1,9-dien-3-yl benzoate (3c)

^{1}H-NMR

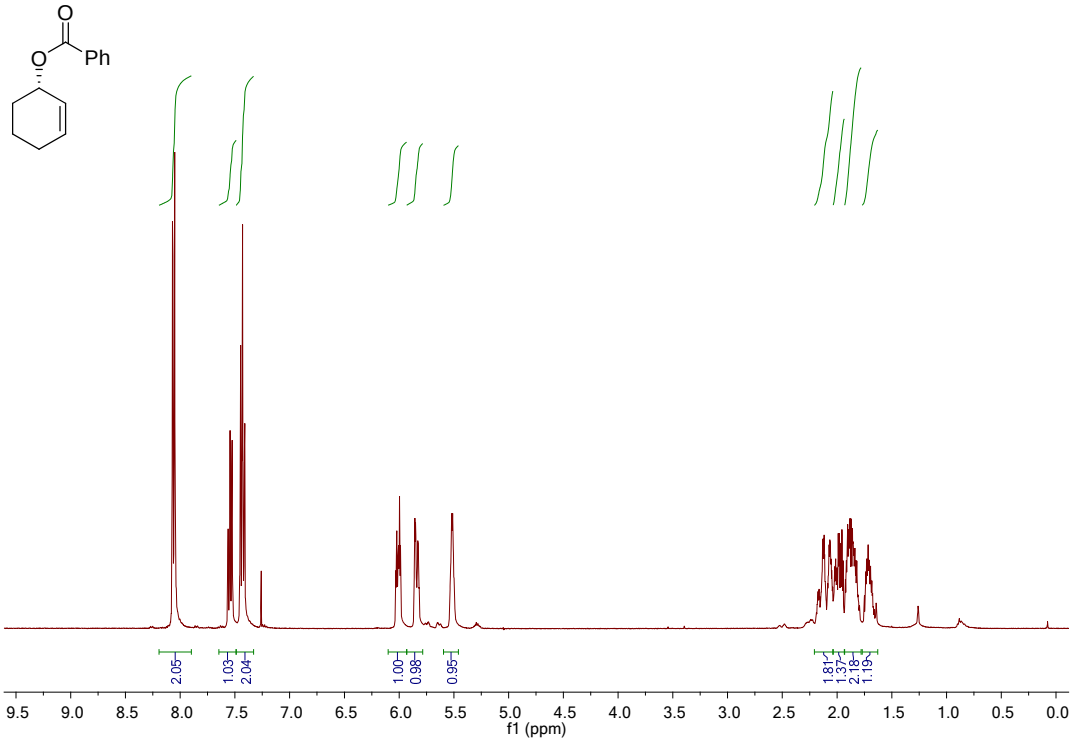


^{13}C-NMR

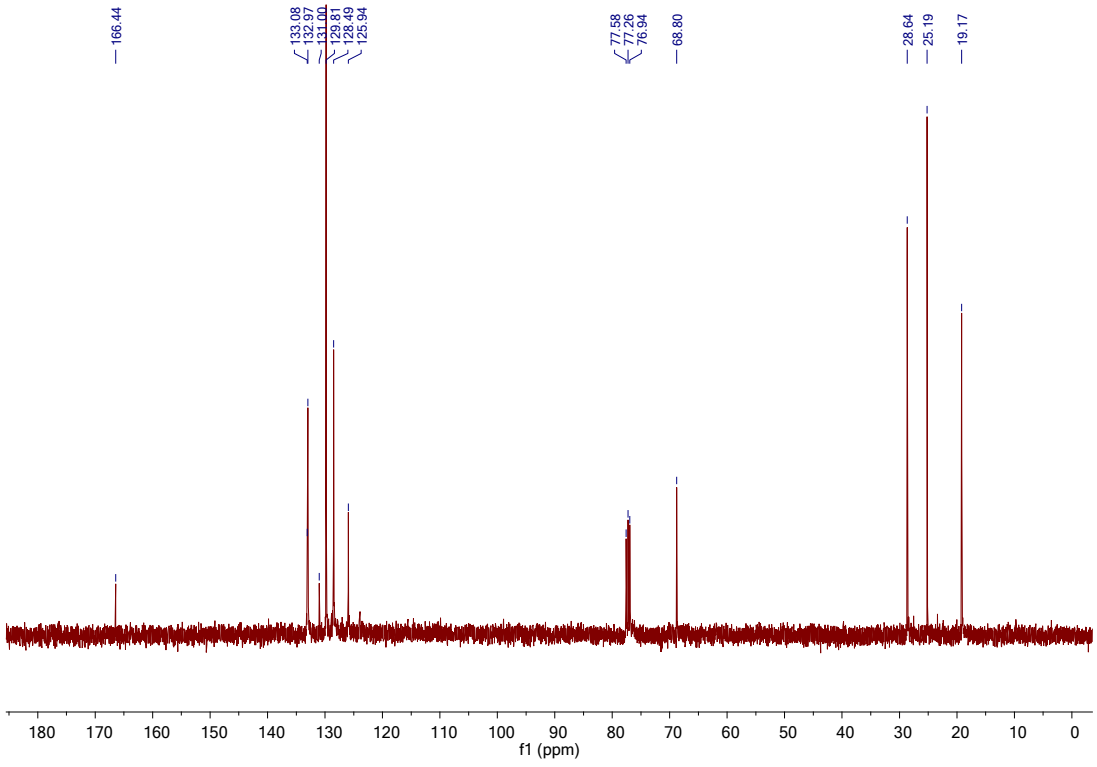


(-)-(*S*)-cyclohex-2-en-1-yl benzoate (4b)

^{1}H-NMR

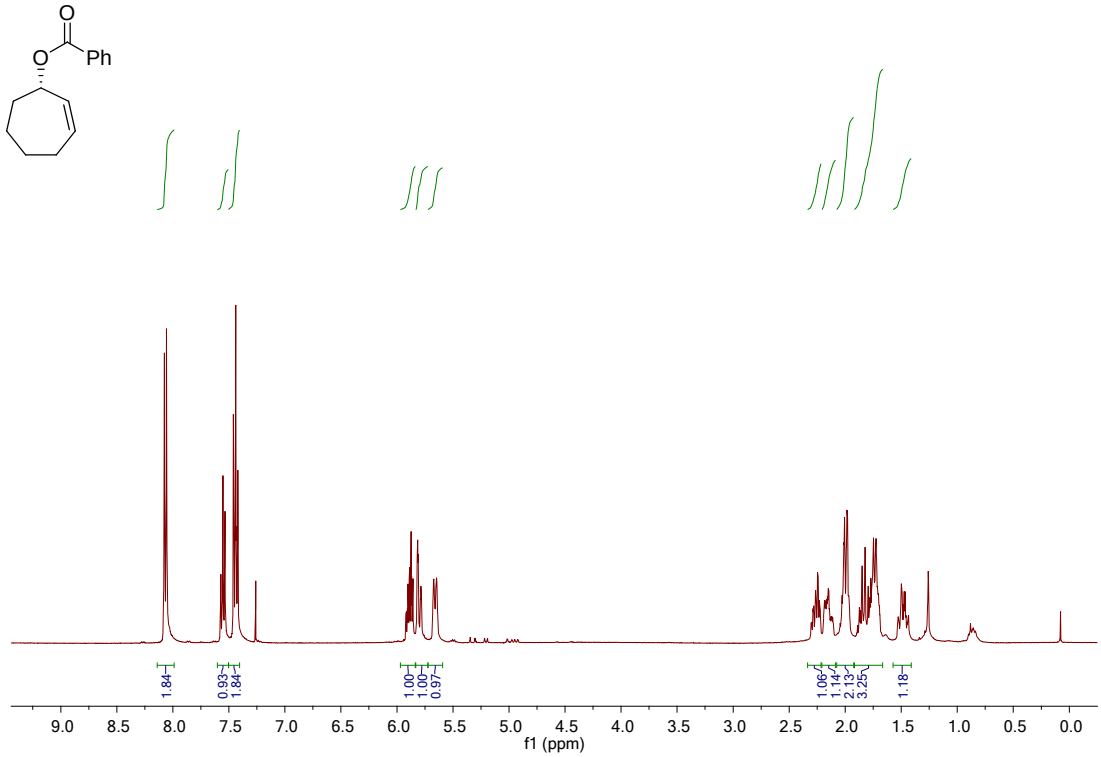


^{13}C-NMR

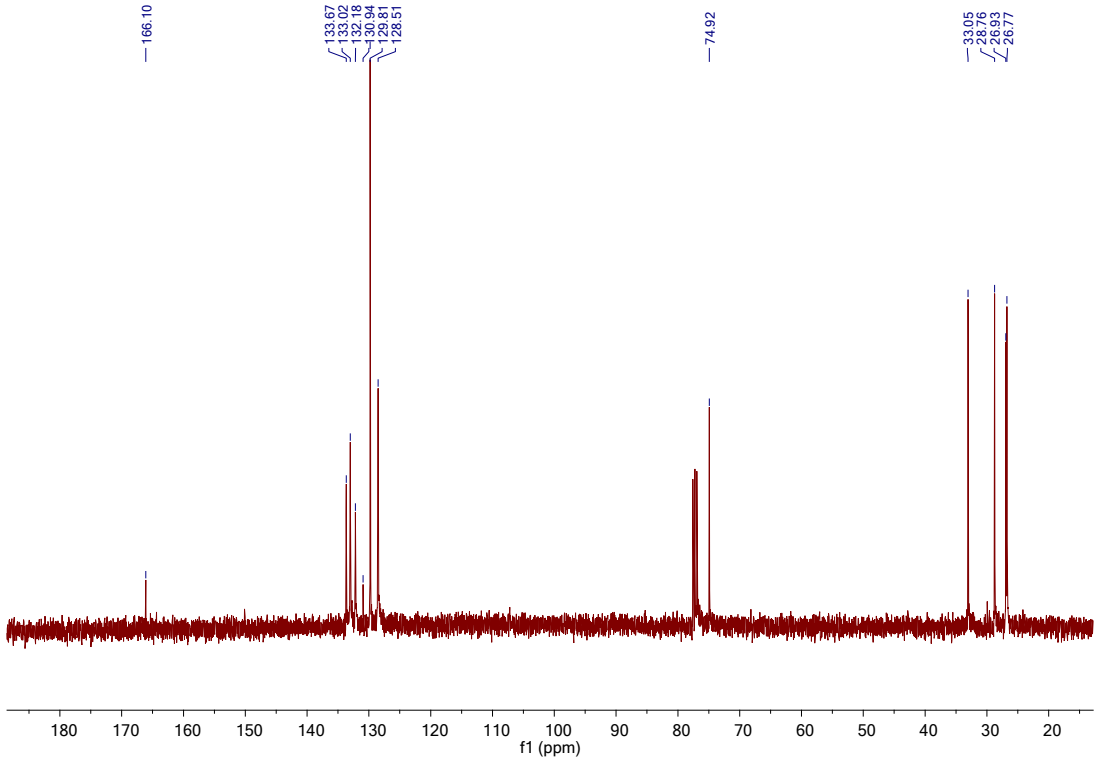


(-)-(*S*)-Cyclohept-2-en-1-yl benzoate (4c)

^{1}H-NMR

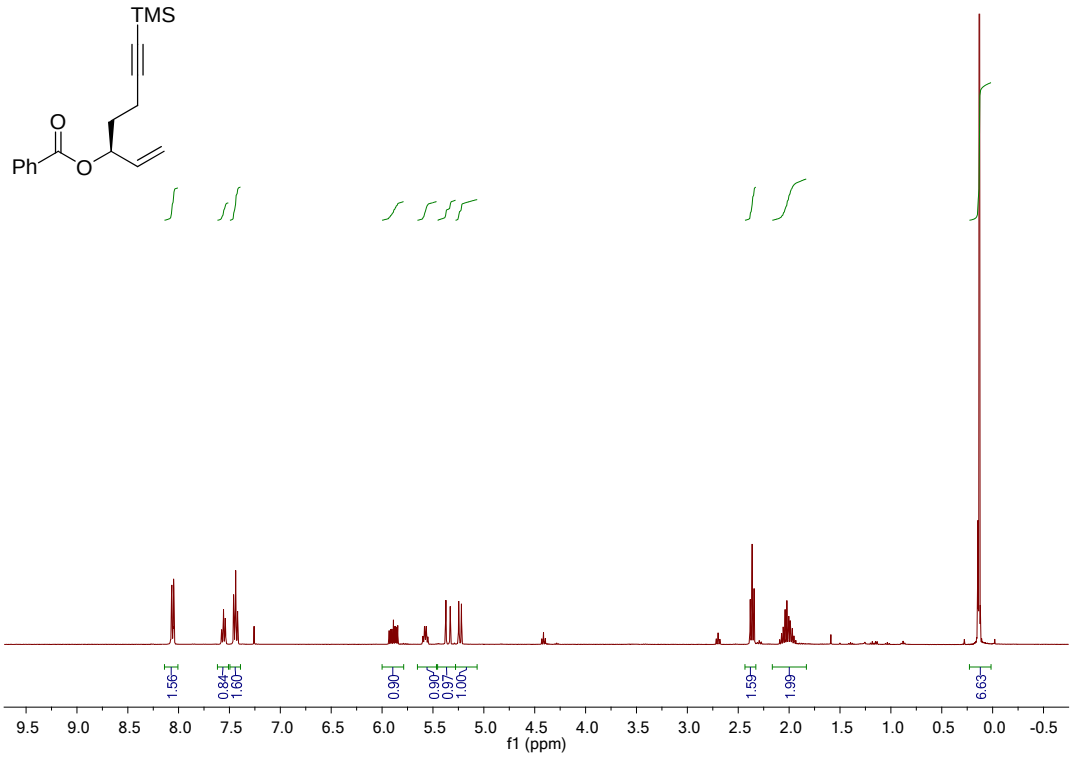


^{13}C-NMR

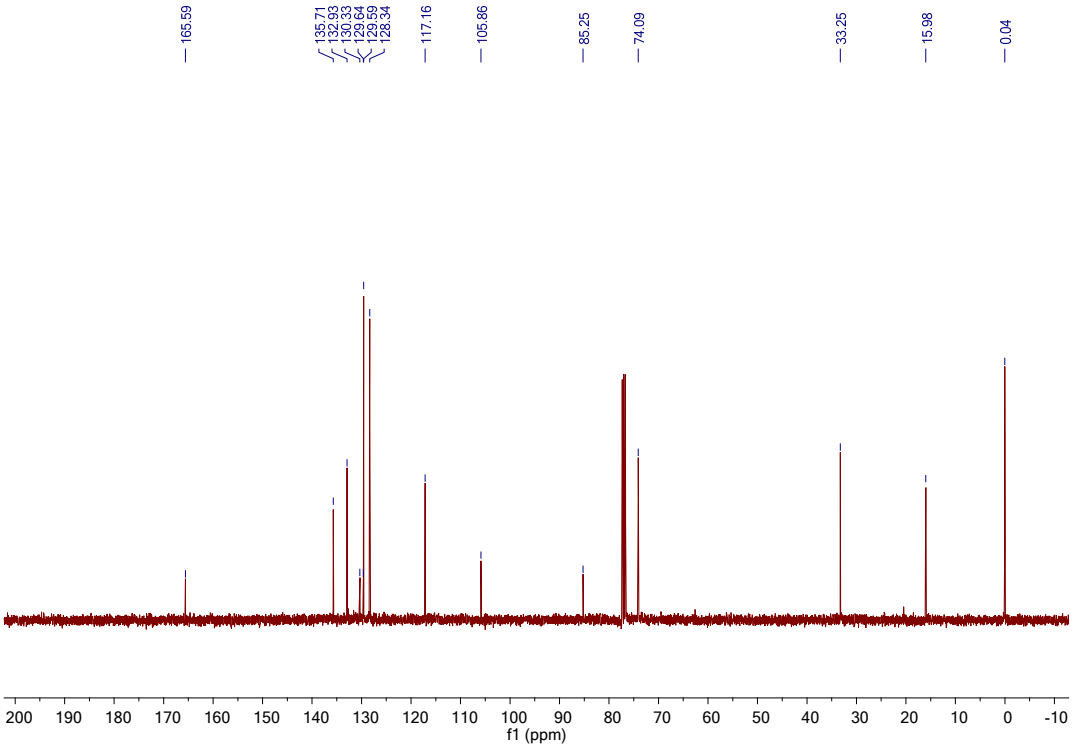


(+)-(*S*)-7-(Trimethylsilyl)hept-1-en-6-yn-3-yl benzoate (6a)

^{1}H-NMR

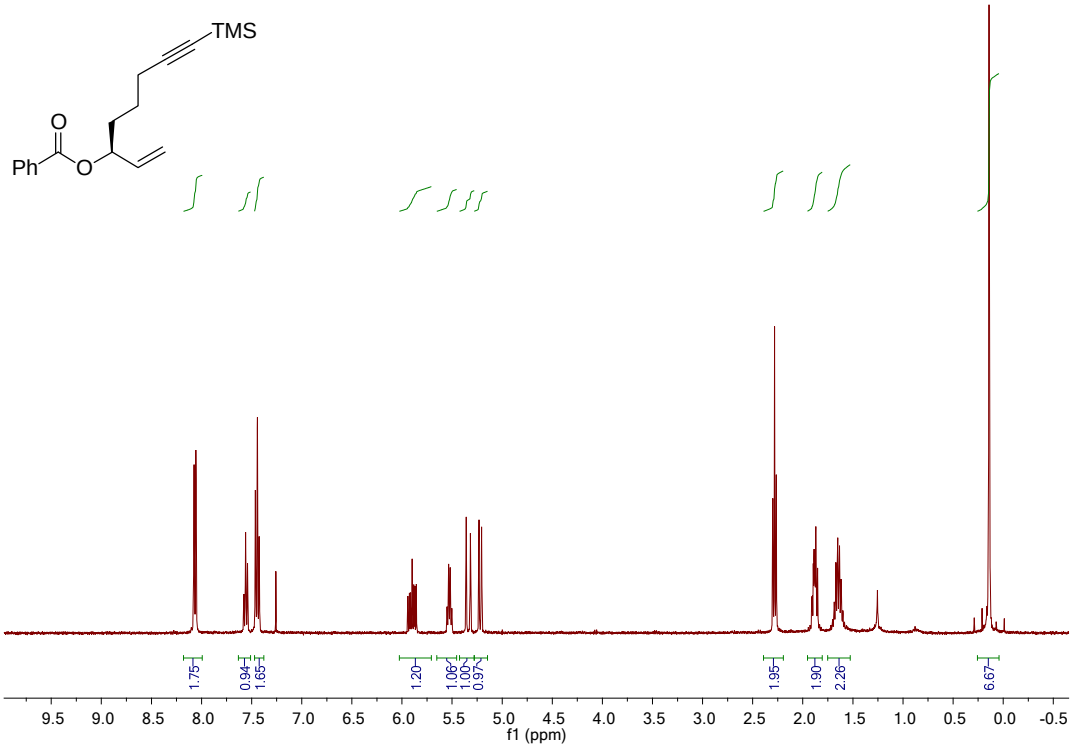


^{13}C-NMR

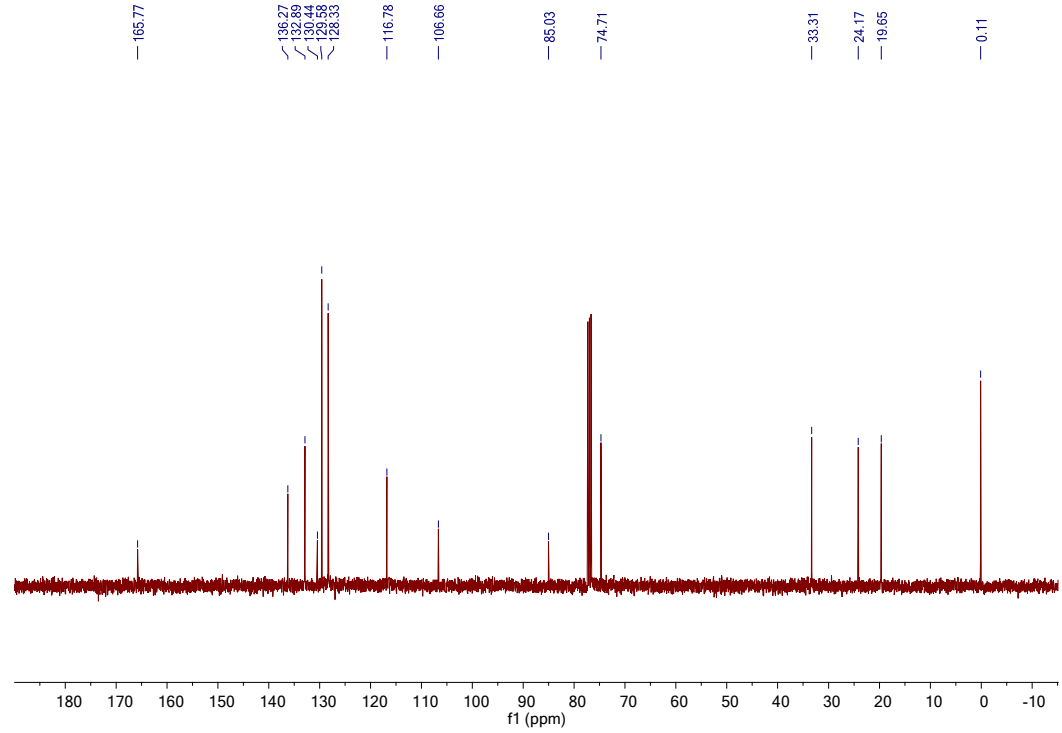


(+)-(*S*)-8-(Trimethylsilyl)oct-1-en-7-yn-3-yl benzoate (6b)

^{1}H-NMR

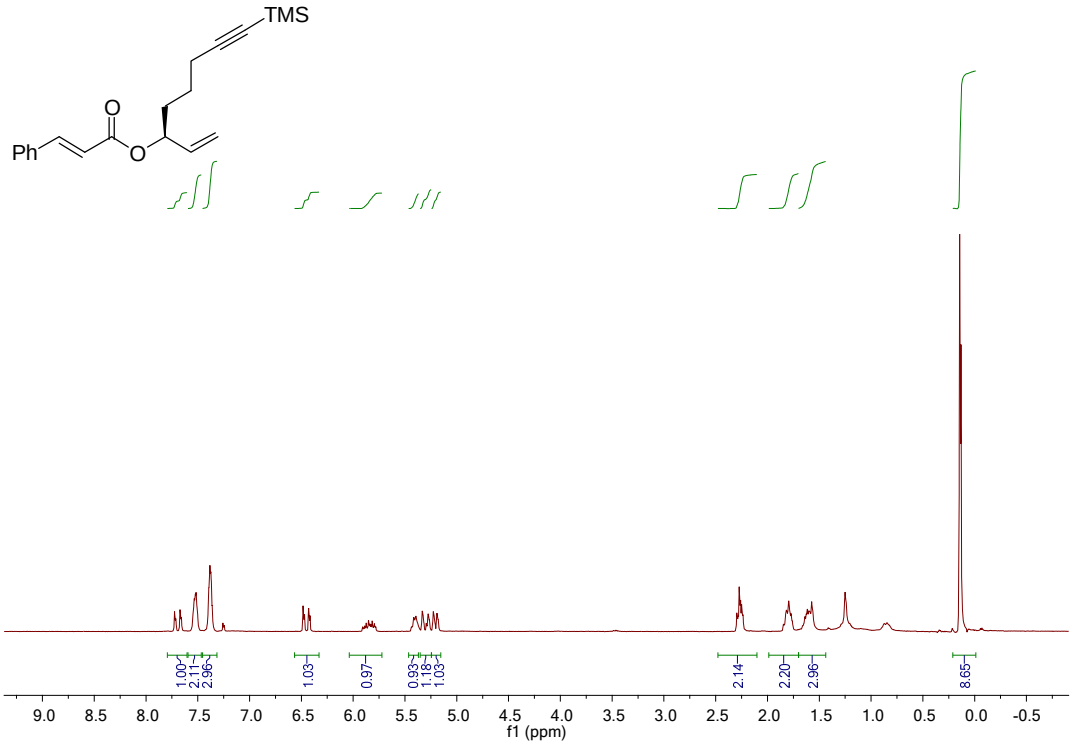


^{13}C-NMR

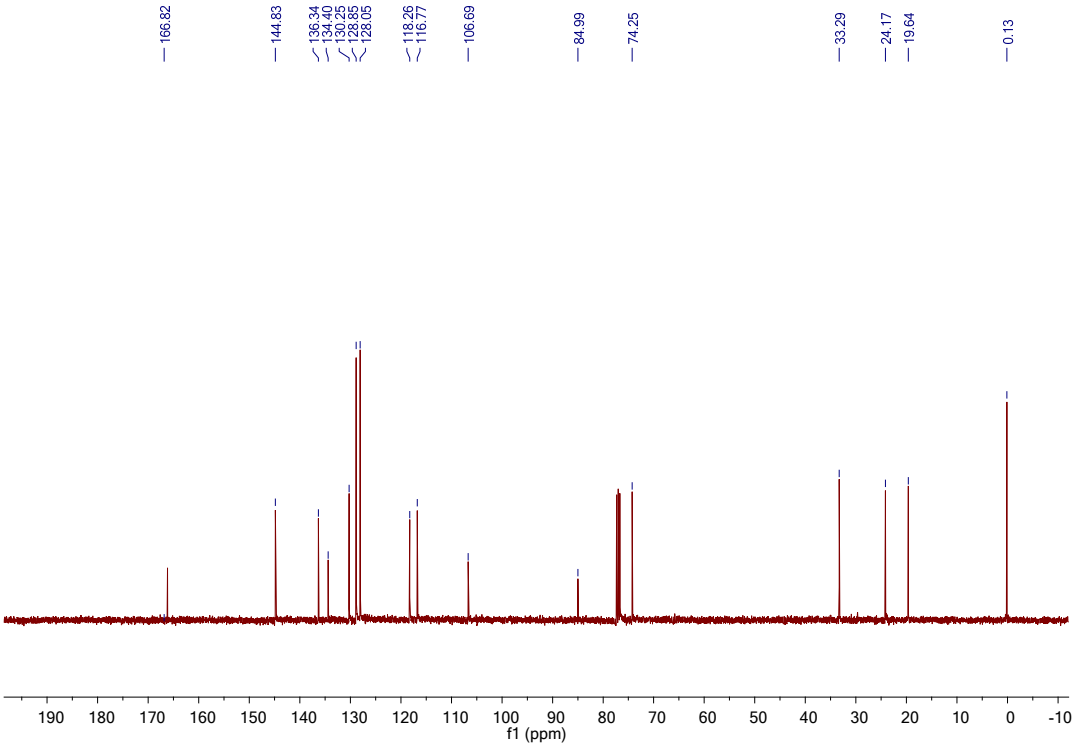


(+)-(*S*)-8-(Trimethylsilyl)oct-1-en-7-yn-3-yl cinnamate (6c)

^{1}H-NMR

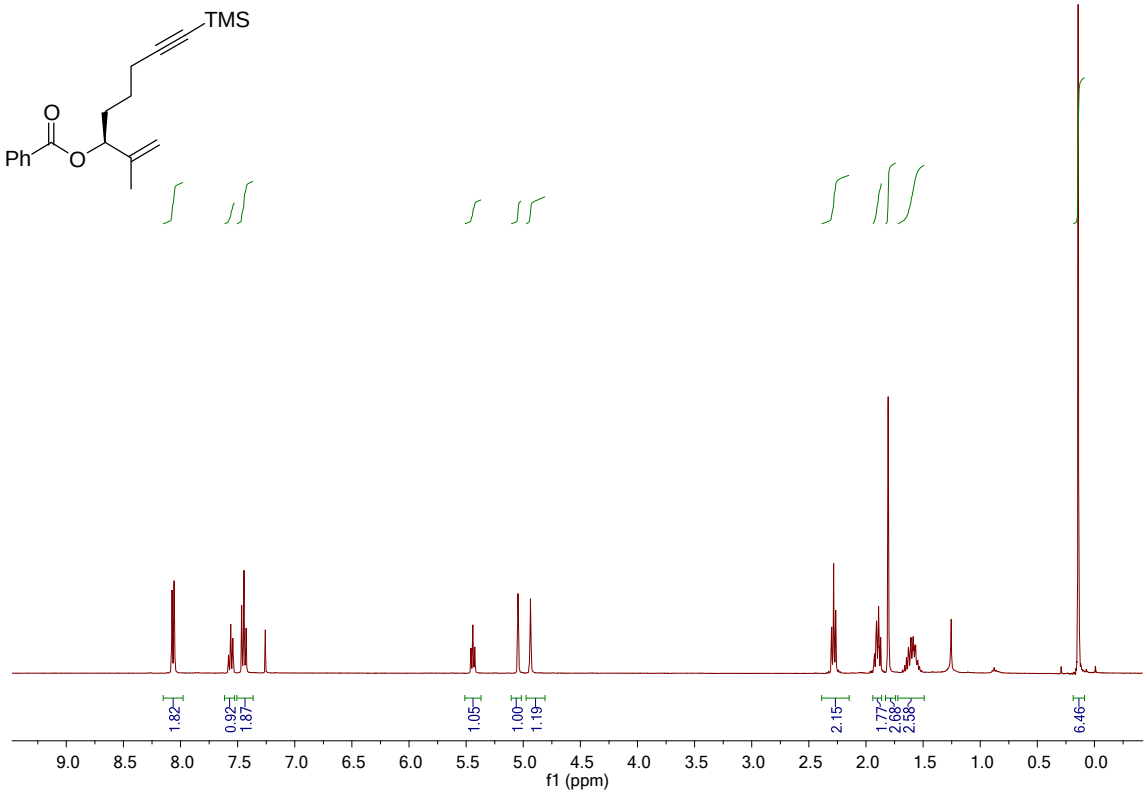


^{13}C-NMR

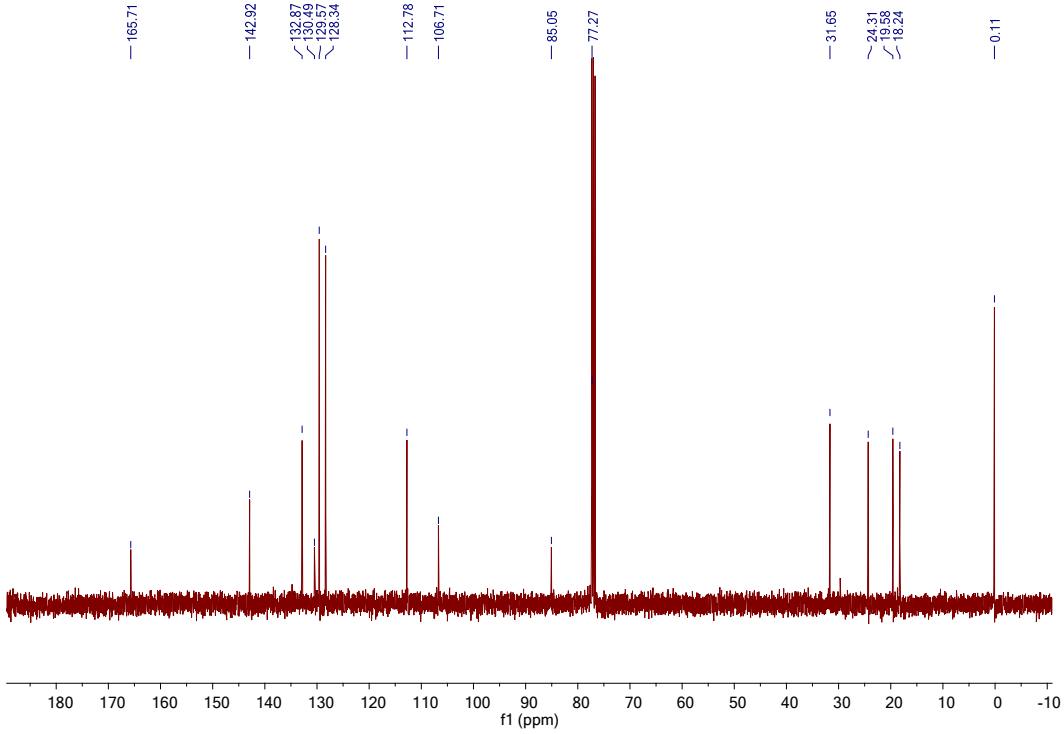


(+)-(*S*)-2-Methyl-8-(trimethylsilyl)oct-1-en-7-yn-3-yl benzoate (6d)

^{1}H-NMR

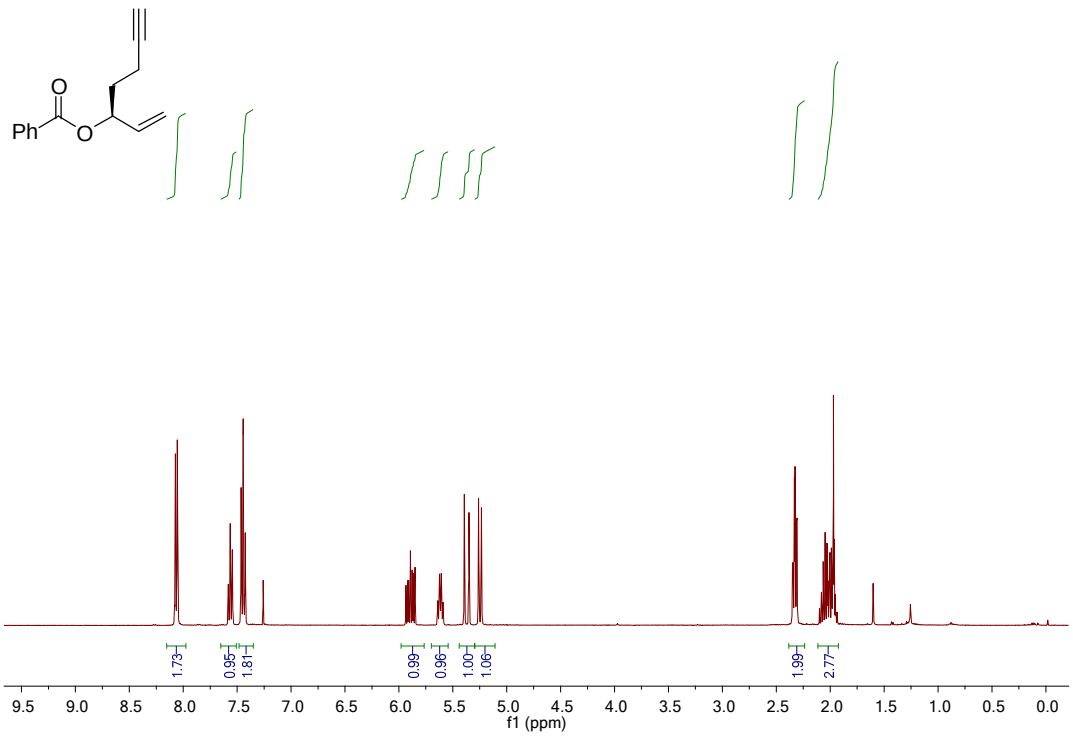


^{13}C-NMR

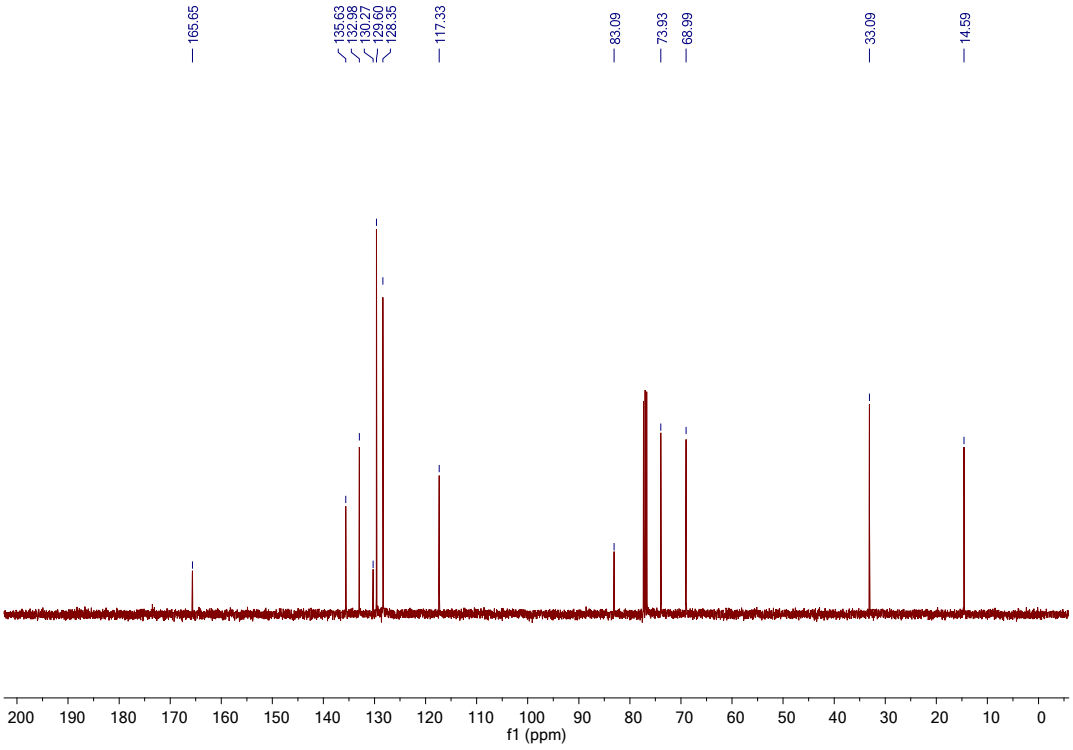


(+)-(*S*)-Hept-1-en-6-yn-3-yl benzoate (7a)

^{1}H-NMR

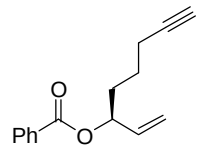


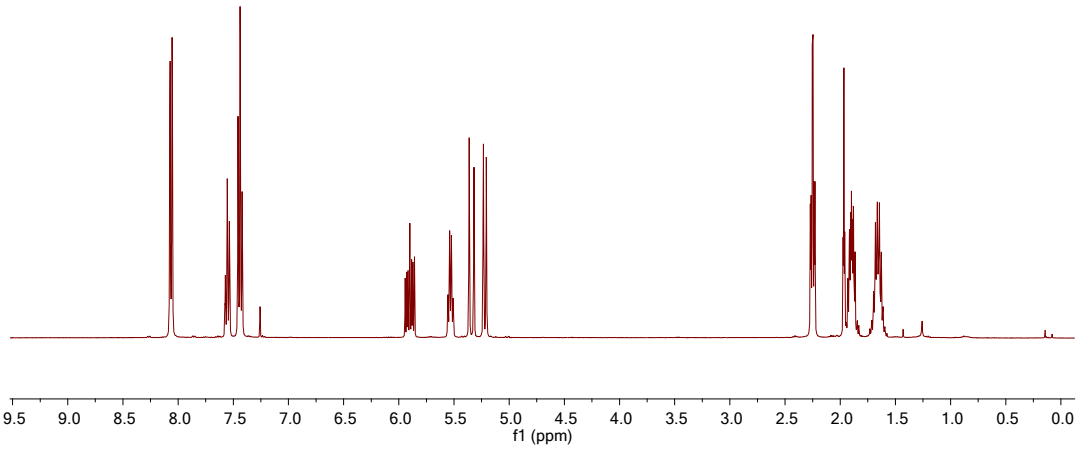
^{13}C-NMR



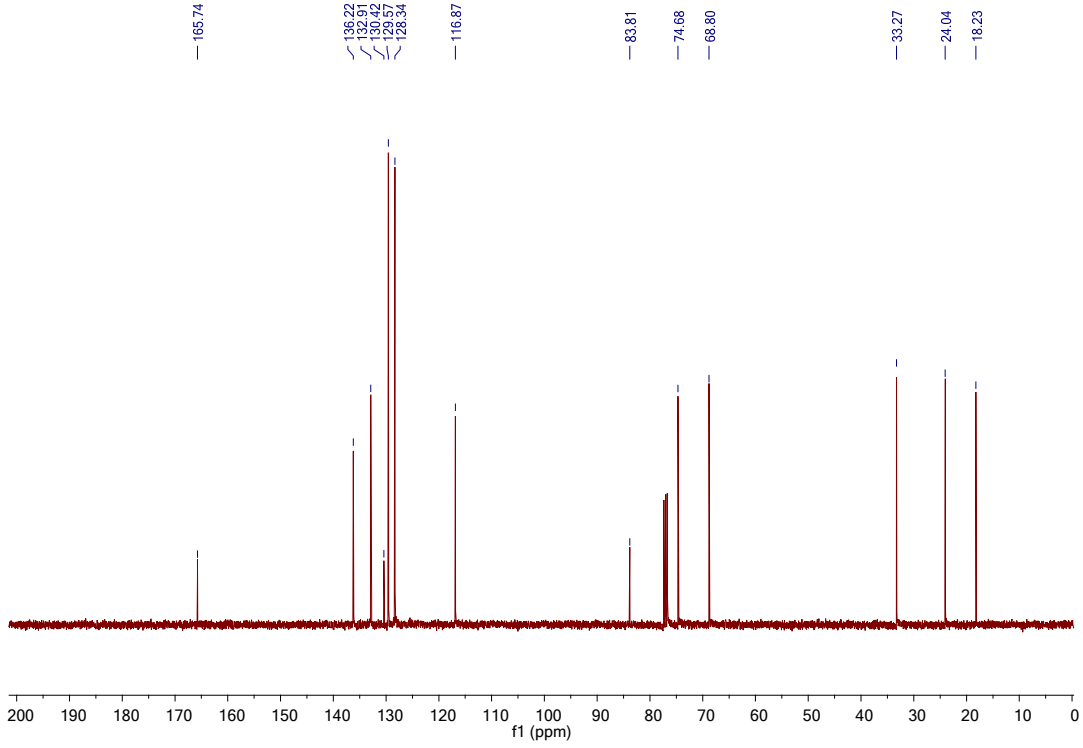
(+)-(*S*)-Oct-1-en-7-yn-3-yl benzoate (7b)

^{1}H-NMR



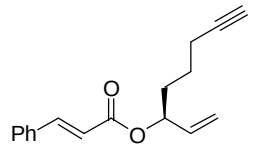


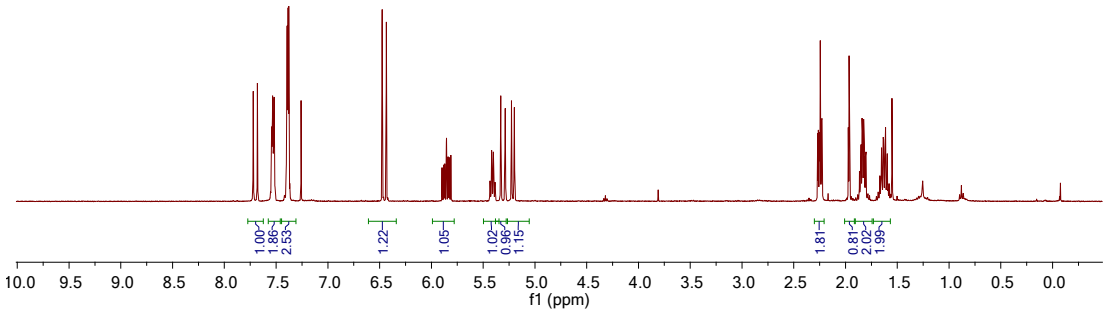
^{13}C-NMR



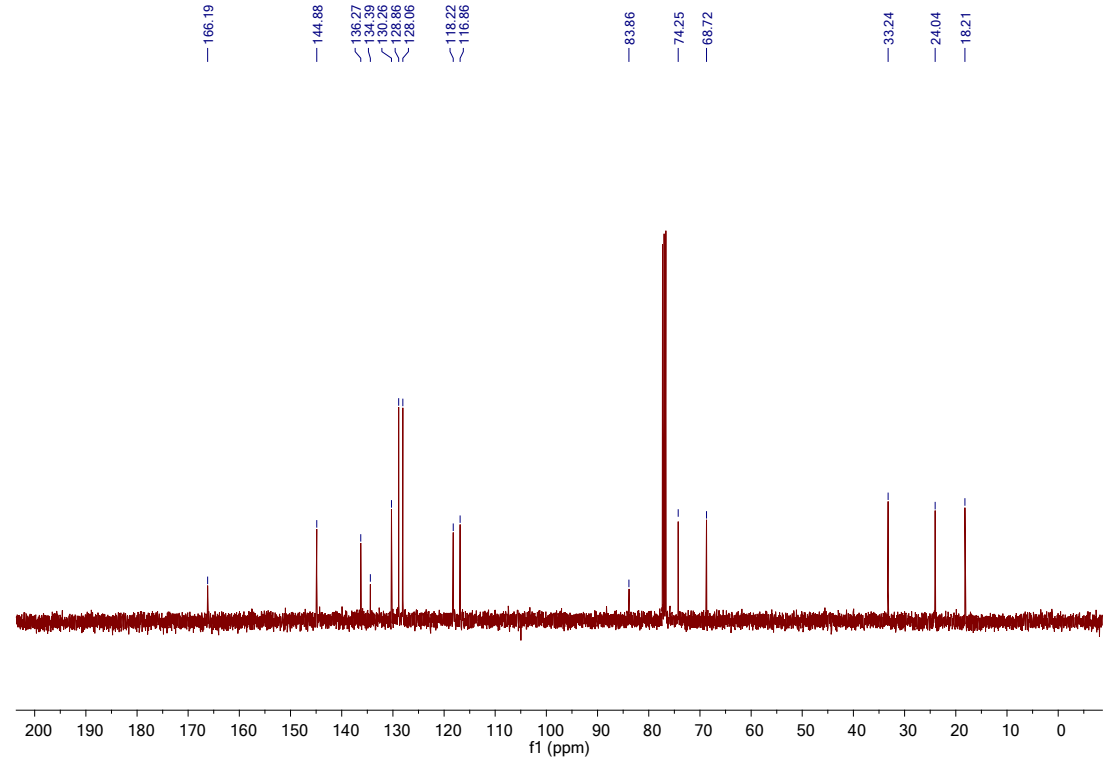
(+)-(*S*)-Oct-1-en-7-yn-3-yl cinnamate (7c)

^{1}H-NMR



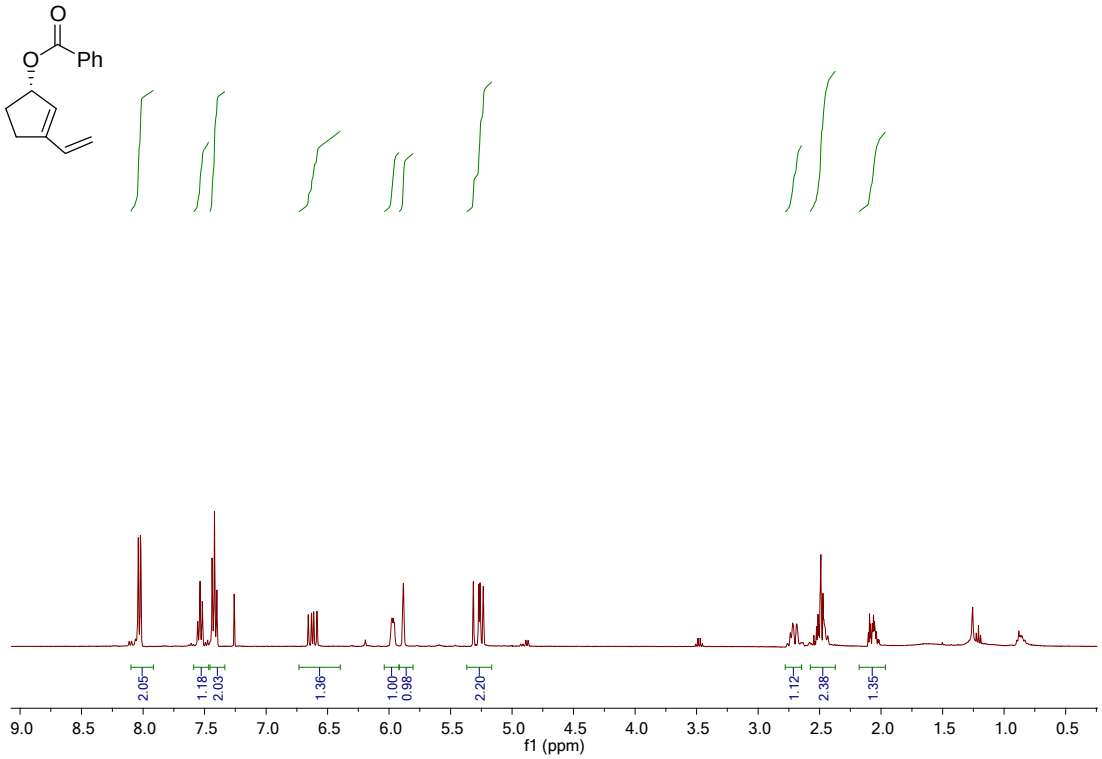


^{13}C-NMR

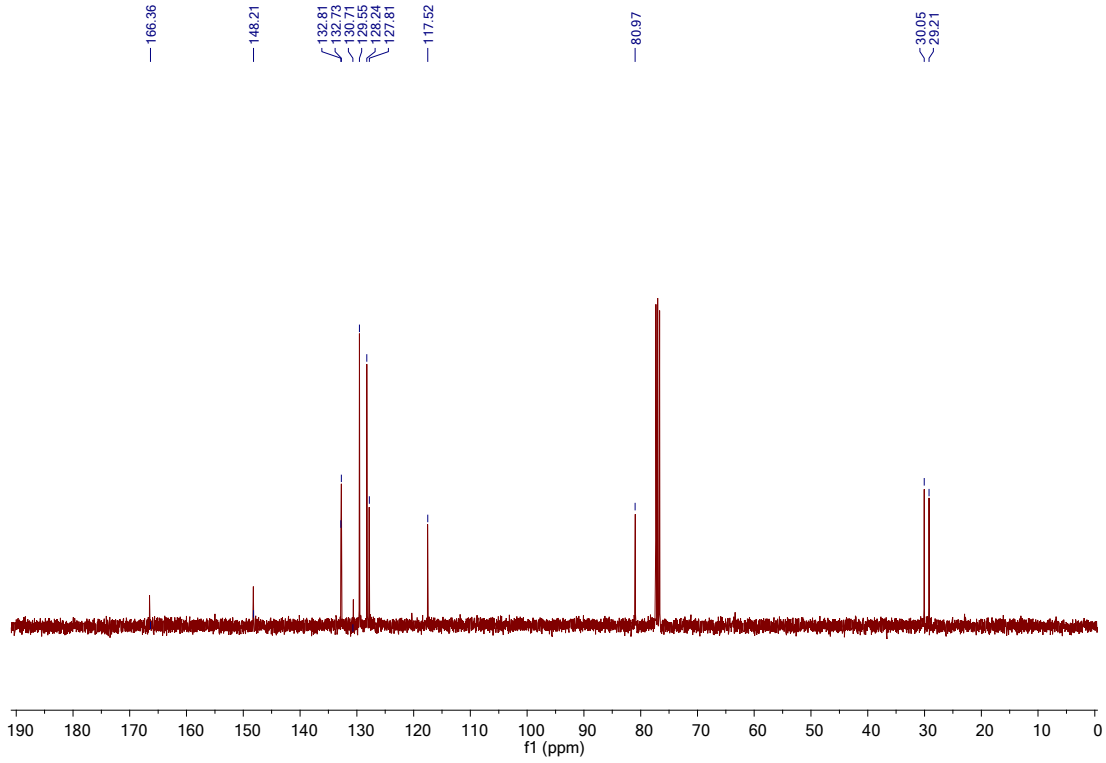


(-)-(*S*)-3-Vinylcyclopent-2-en-1-yl benzoate (8a)

^{1}H-NMR

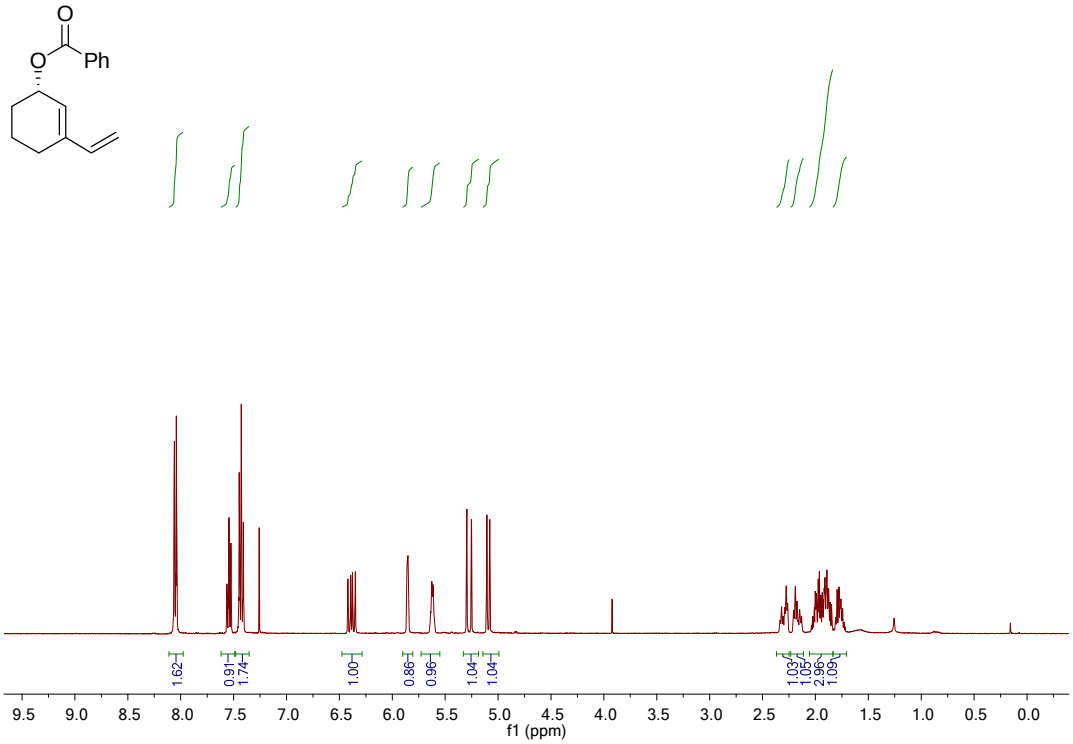


^{13}C-NMR

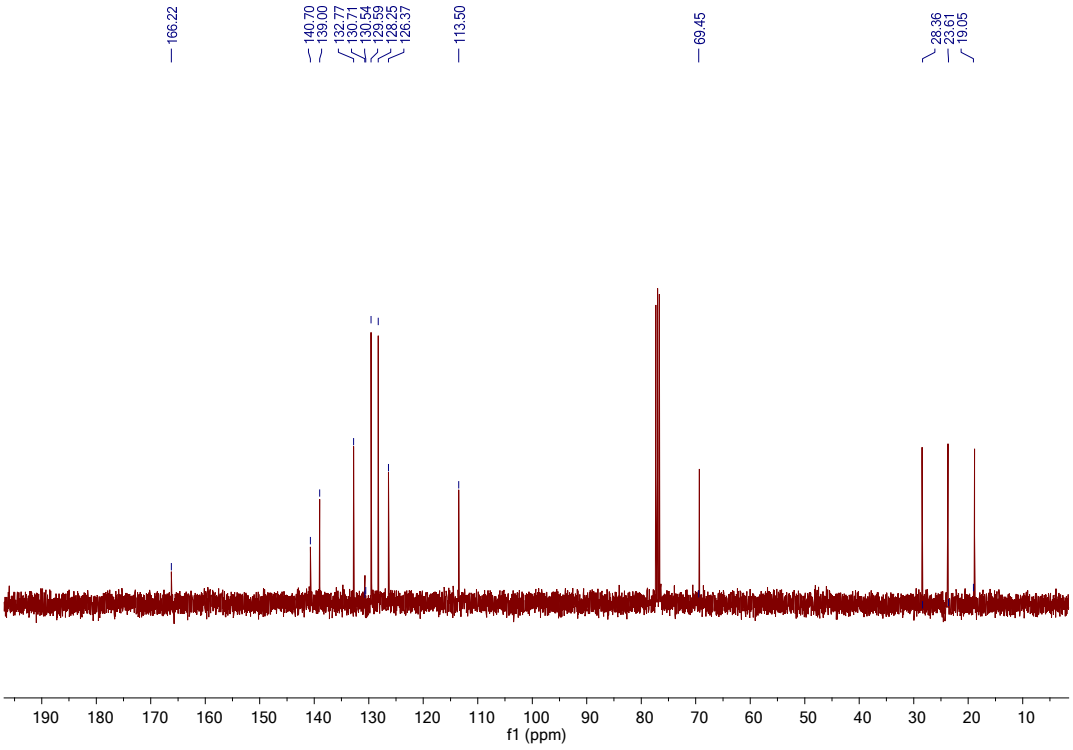


(-)-(*S*)-3-Vinylcyclohex-2-en-1-yl benzoate (8b)

^{1}H-NMR

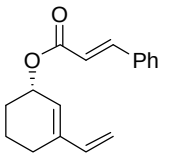


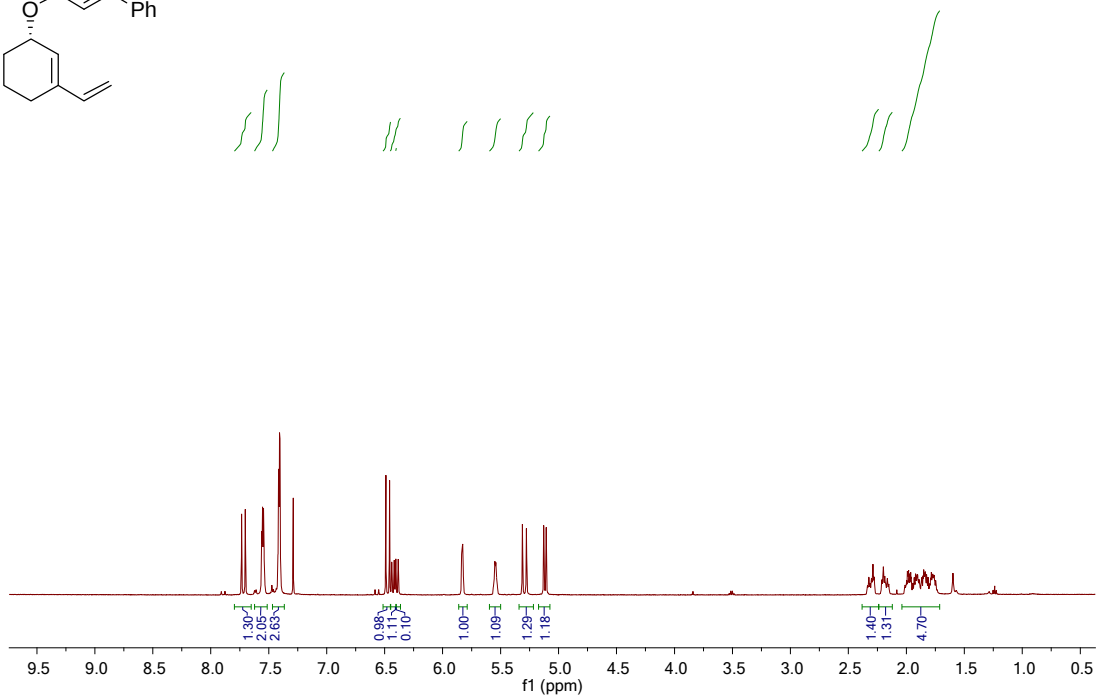
^{13}C-NMR



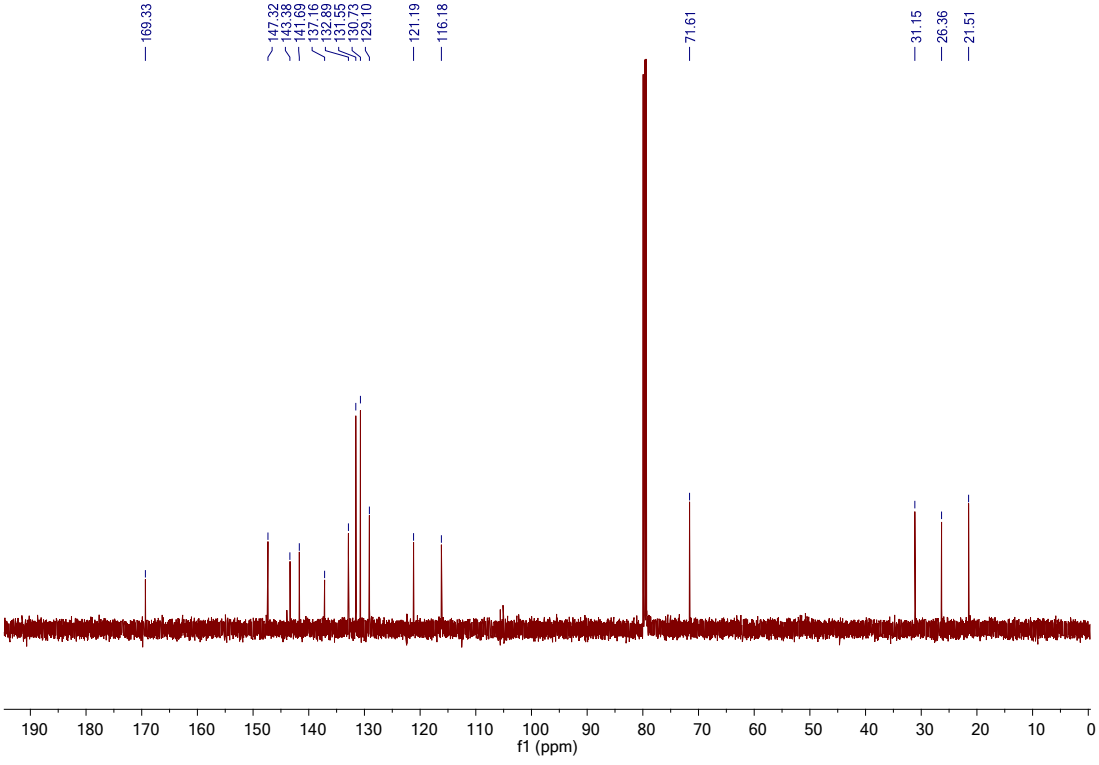
(-)-(*S*)-3-Vinylcyclohex-2-en-1-yl benzoate (8c)

^{1}H-NMR



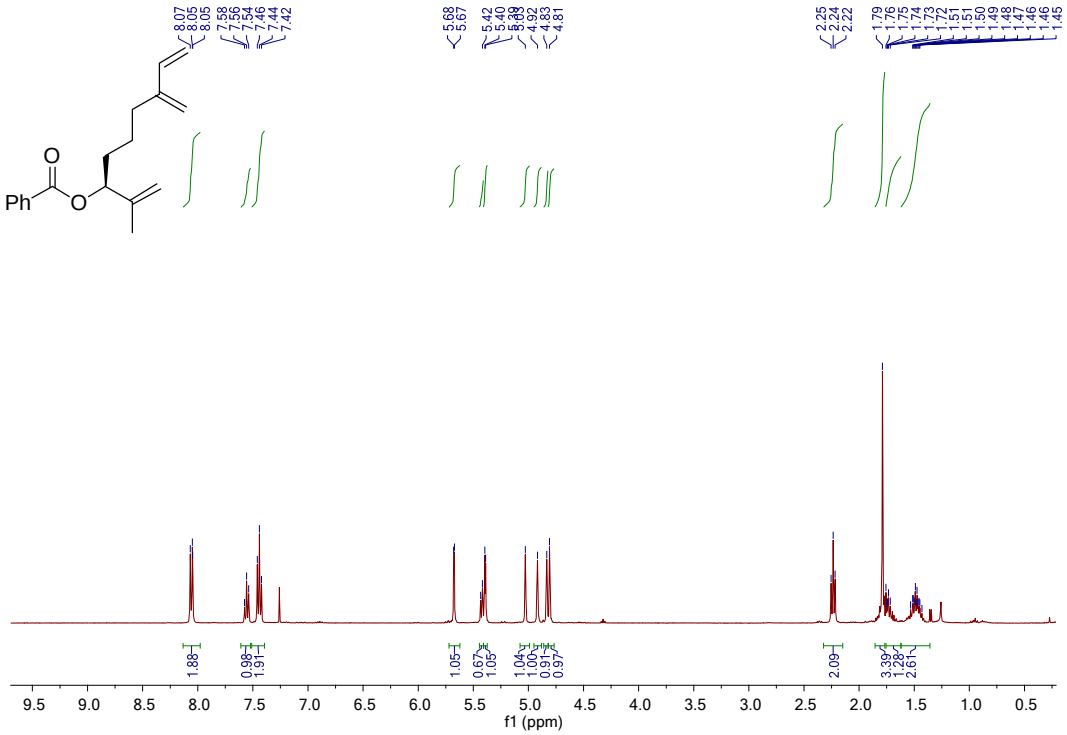


^{13}C-NMR

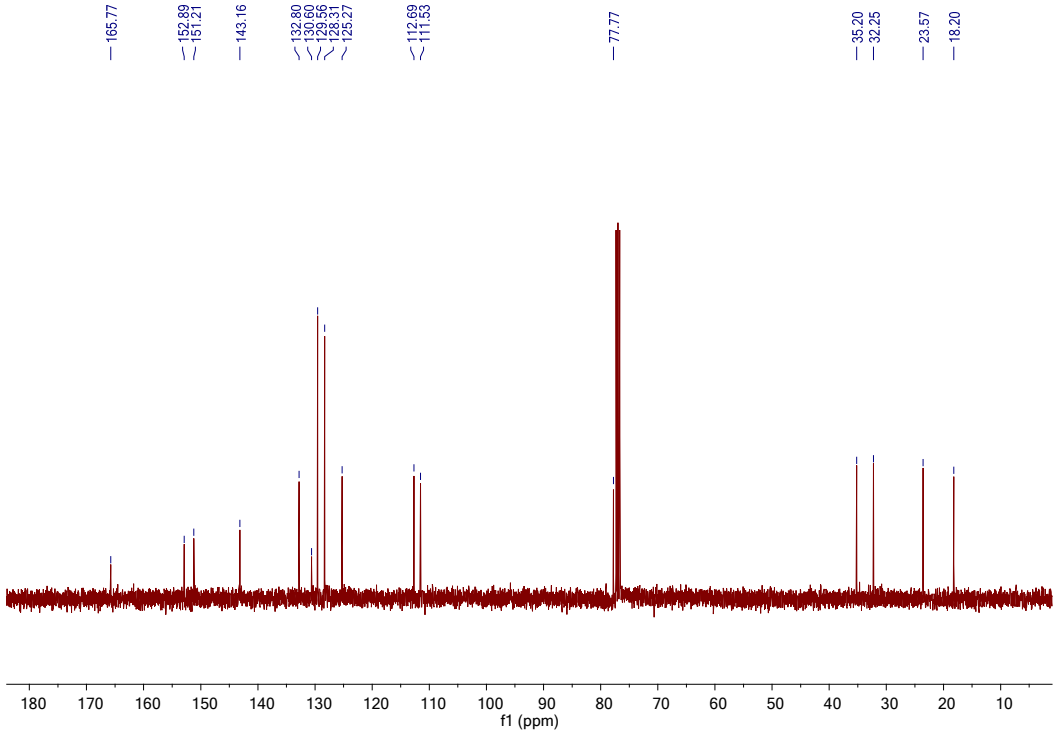


(+)-(*S*)-2-Methyl-7-methylenenona-1,8-dien-3-yl benzoate (8d)

^{1}H-NMR

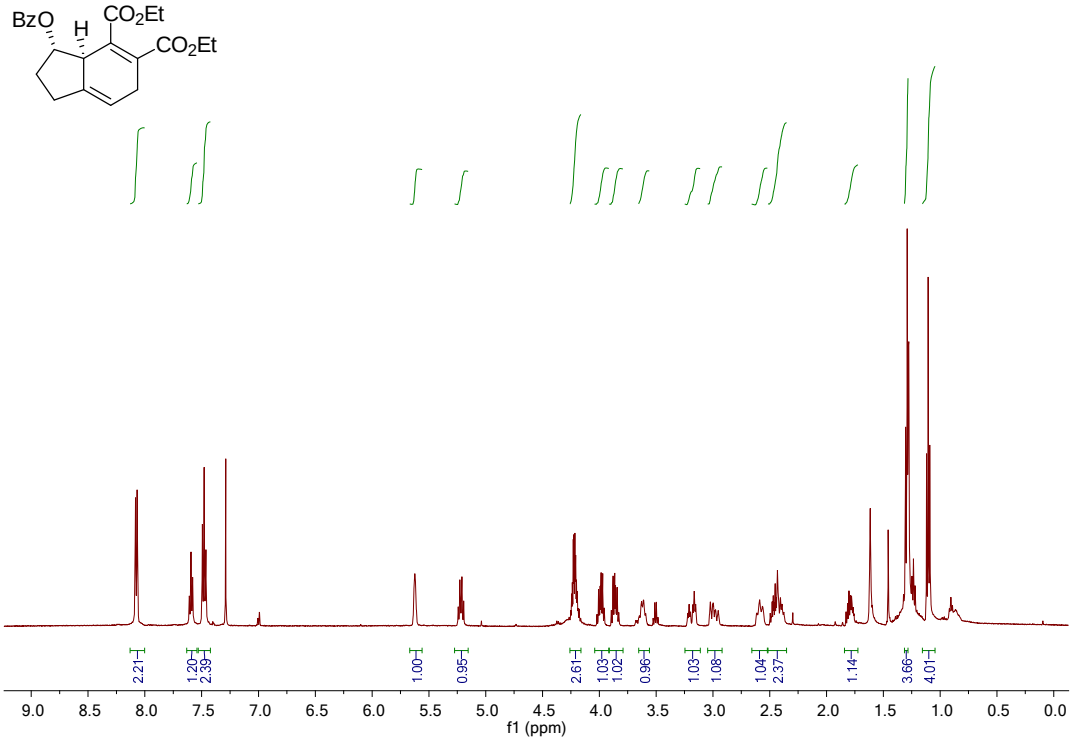


^{13}C-NMR

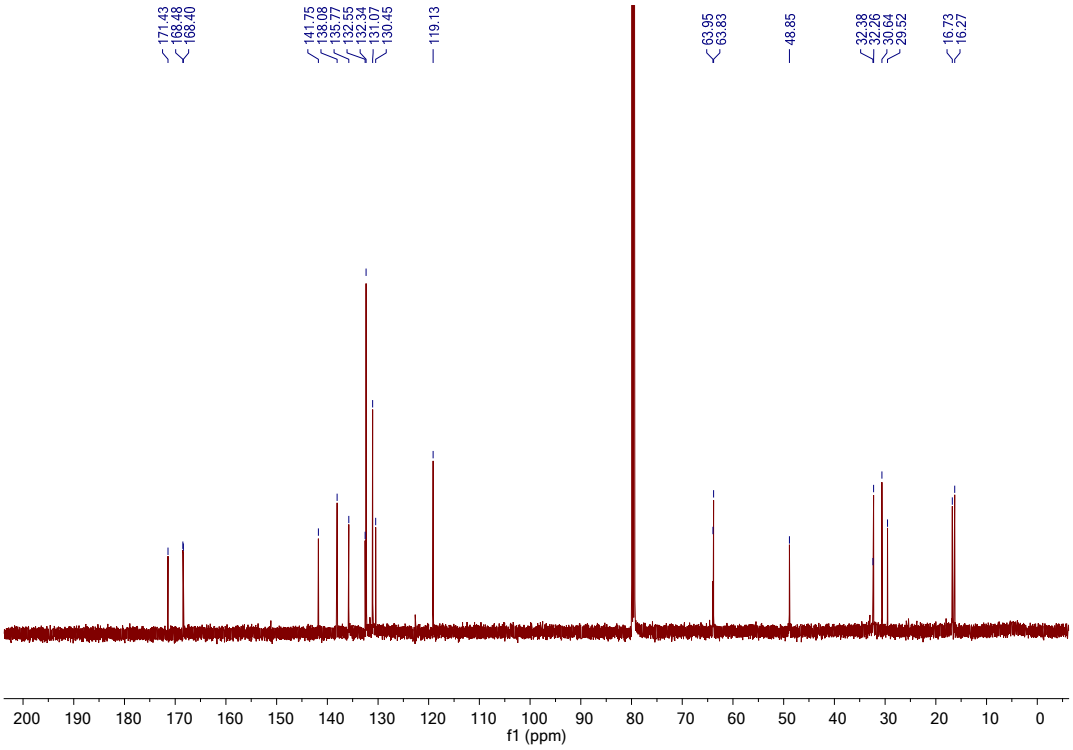


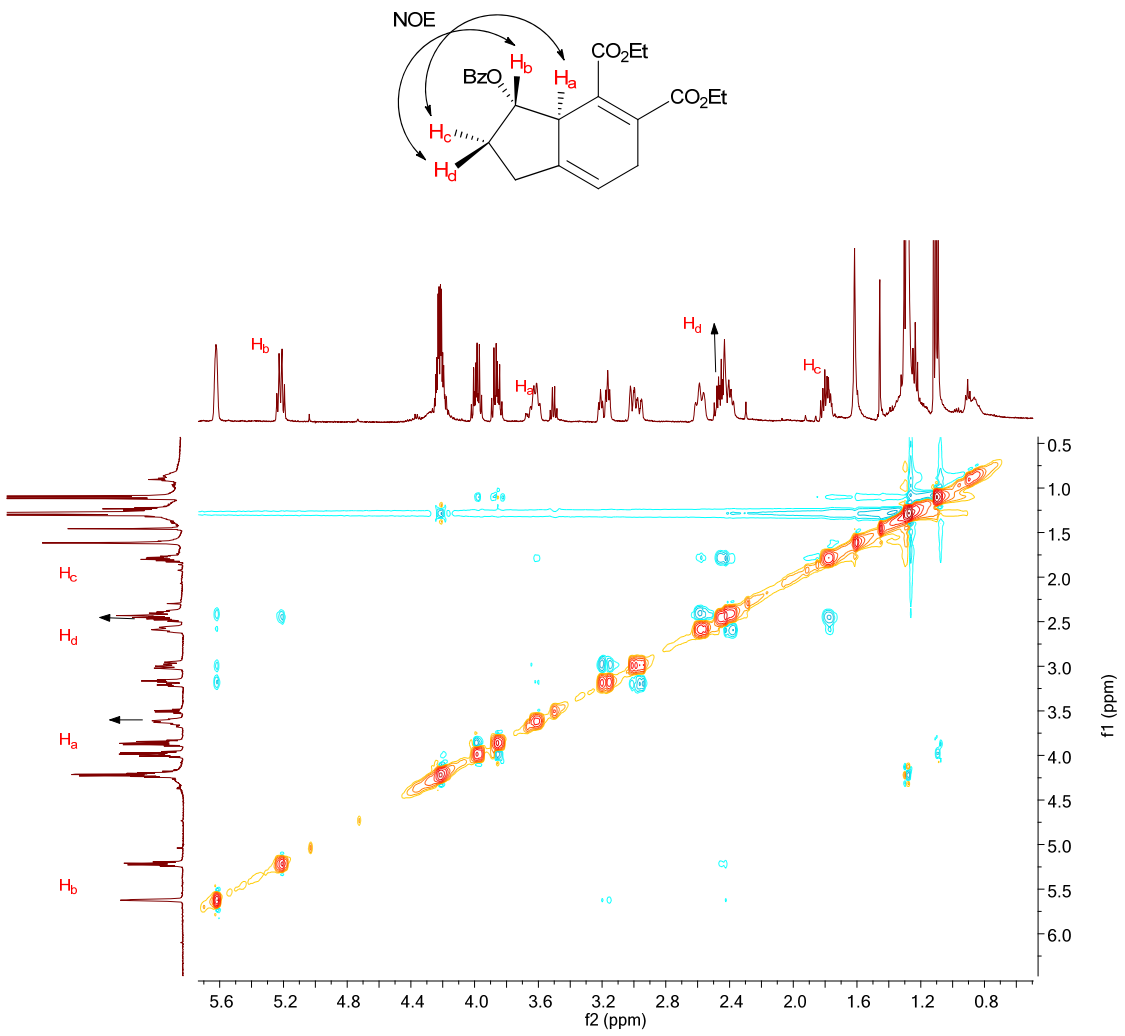
(3*S*,3a*R*)-Diethyl 3-(benzoyloxy)-2,3,3a,6-tetrahydro-1H-indene-4,5-dicarboxylate (9a)

^{1}H-NMR



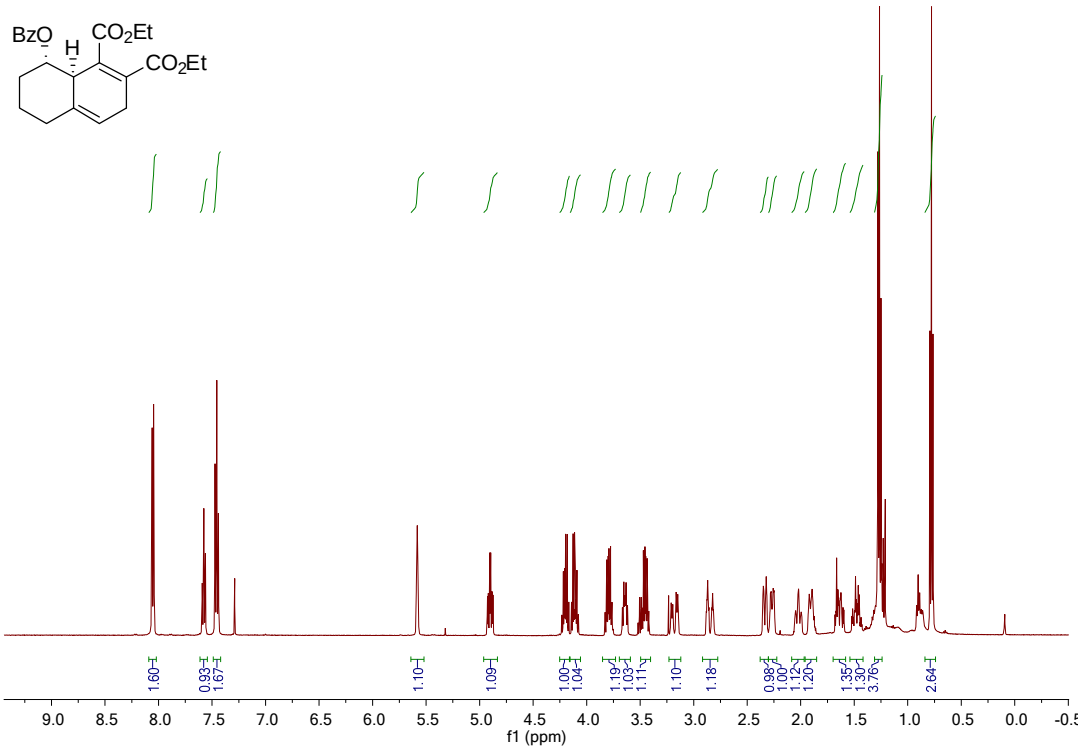
^{13}C-NMR



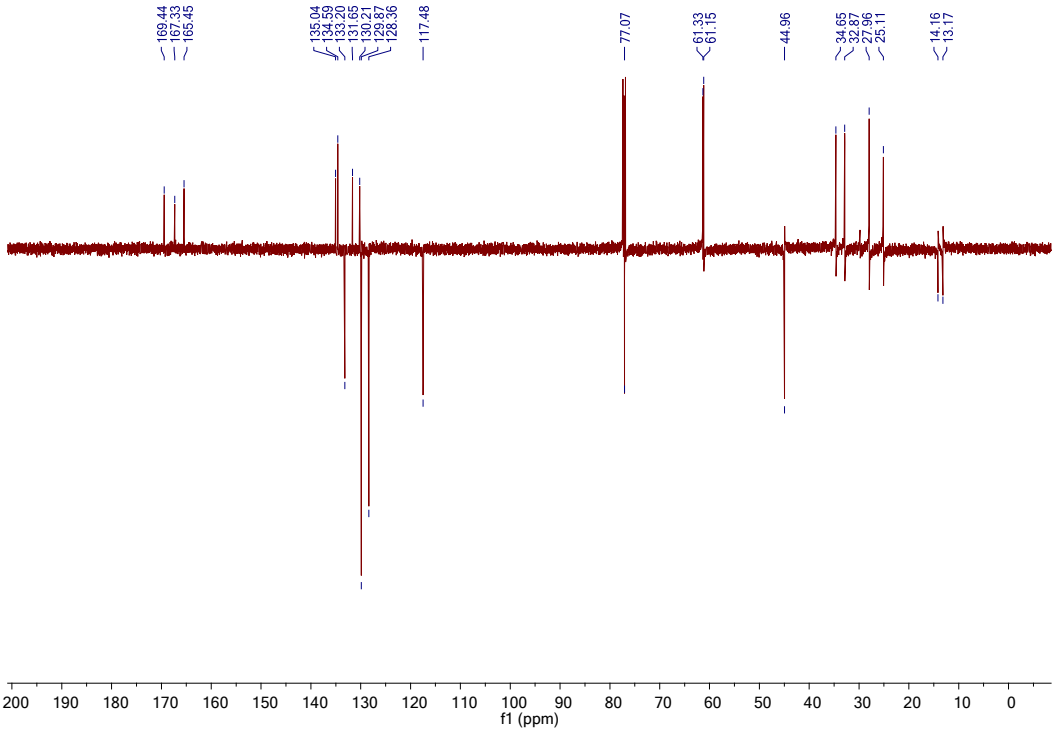

NOE
BzO
H_b
H_a
CO_2Et
CO_2Et
H_c
H_d
H_b
H_a
H_d
H_c
H_c
H_d
H_a
H_b
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
f2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
f1 (ppm)

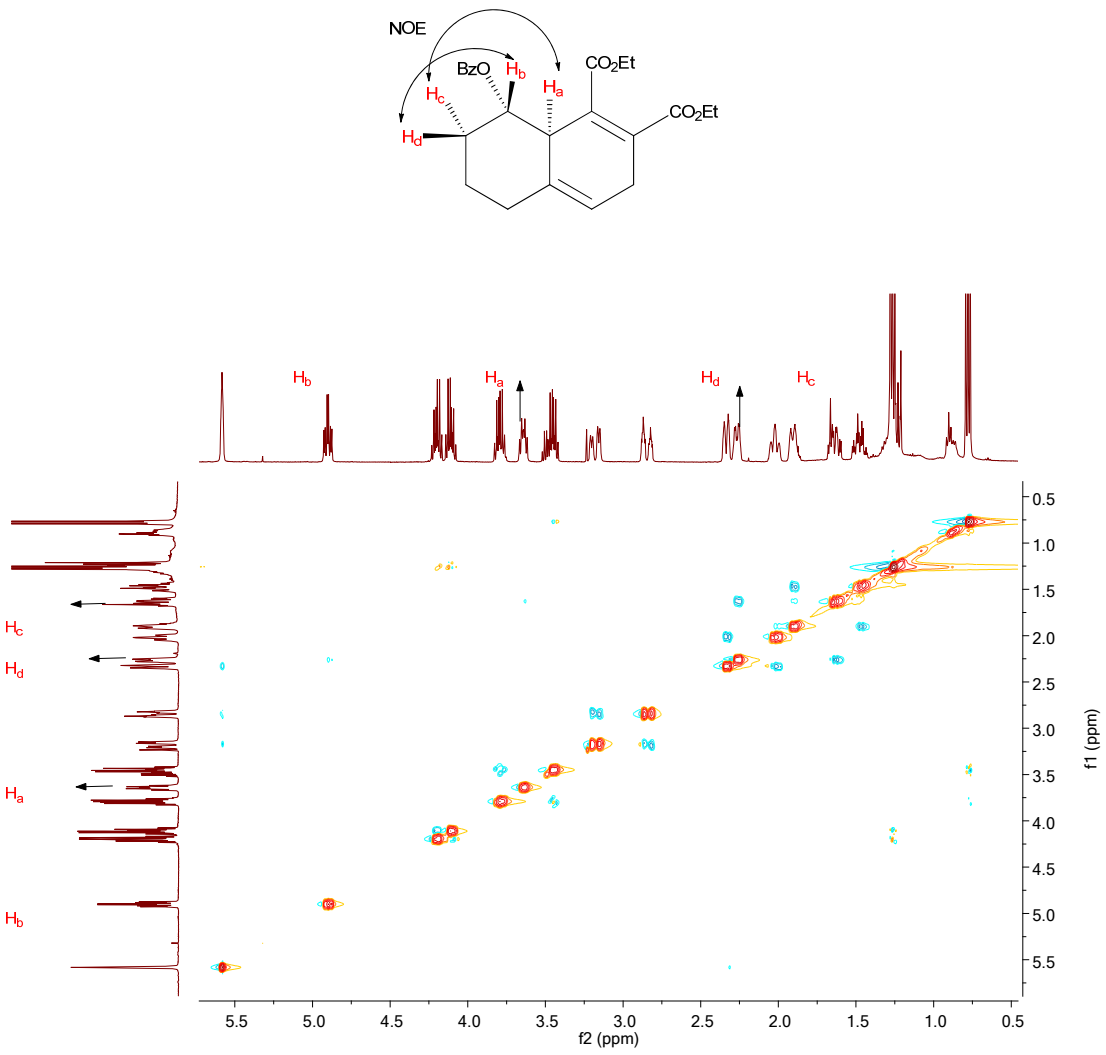
(8*S*,8a*R*)-Diethyl 8-(benzoyloxy)-3,5,6,7,8,8a-hexahydronaphthalene -1,2-dicarboxylate (9b)

^{1}H-NMR



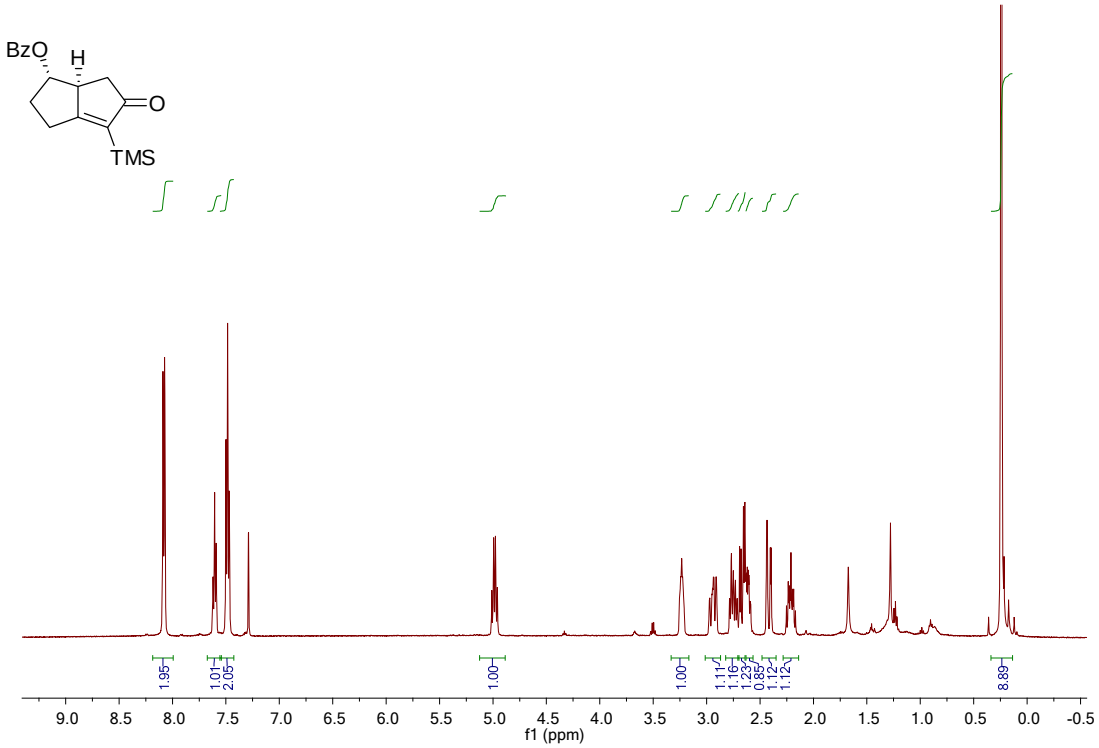
APT-NMR



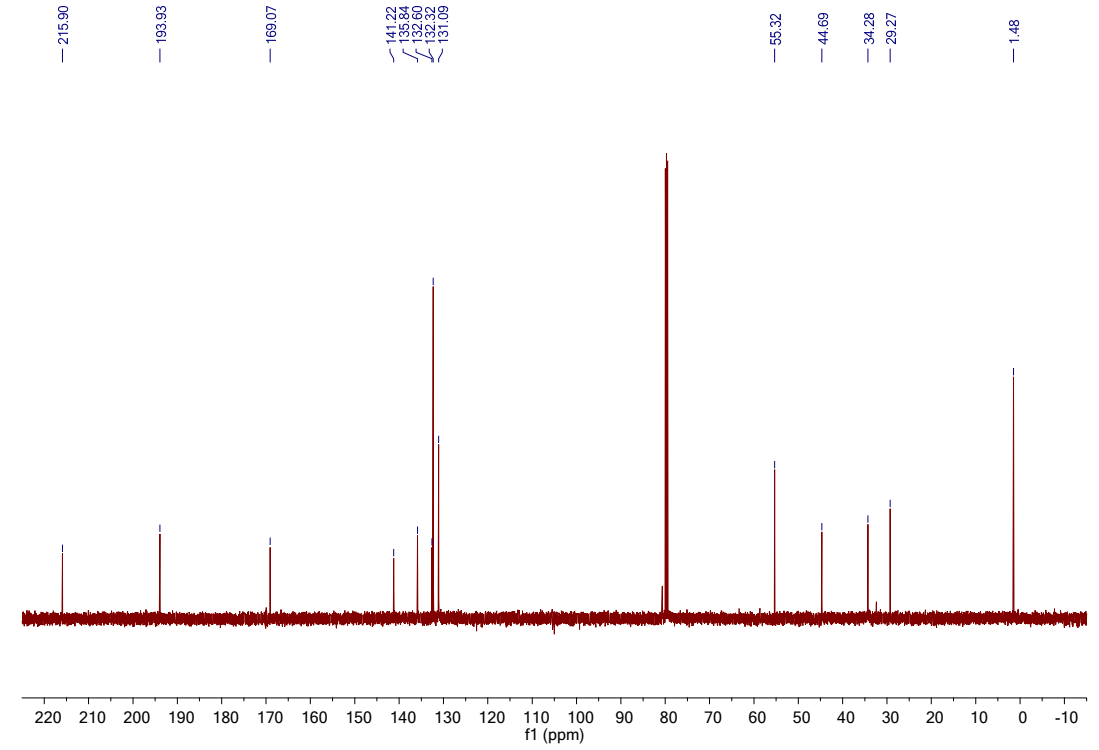

NOE
BzO
Hb
Ha
Hc
Hd
CO2Et
CO2Et
Hb
Ha
Hd
Hc
Hc
Hd
Ha
Hb
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
f1 (ppm)

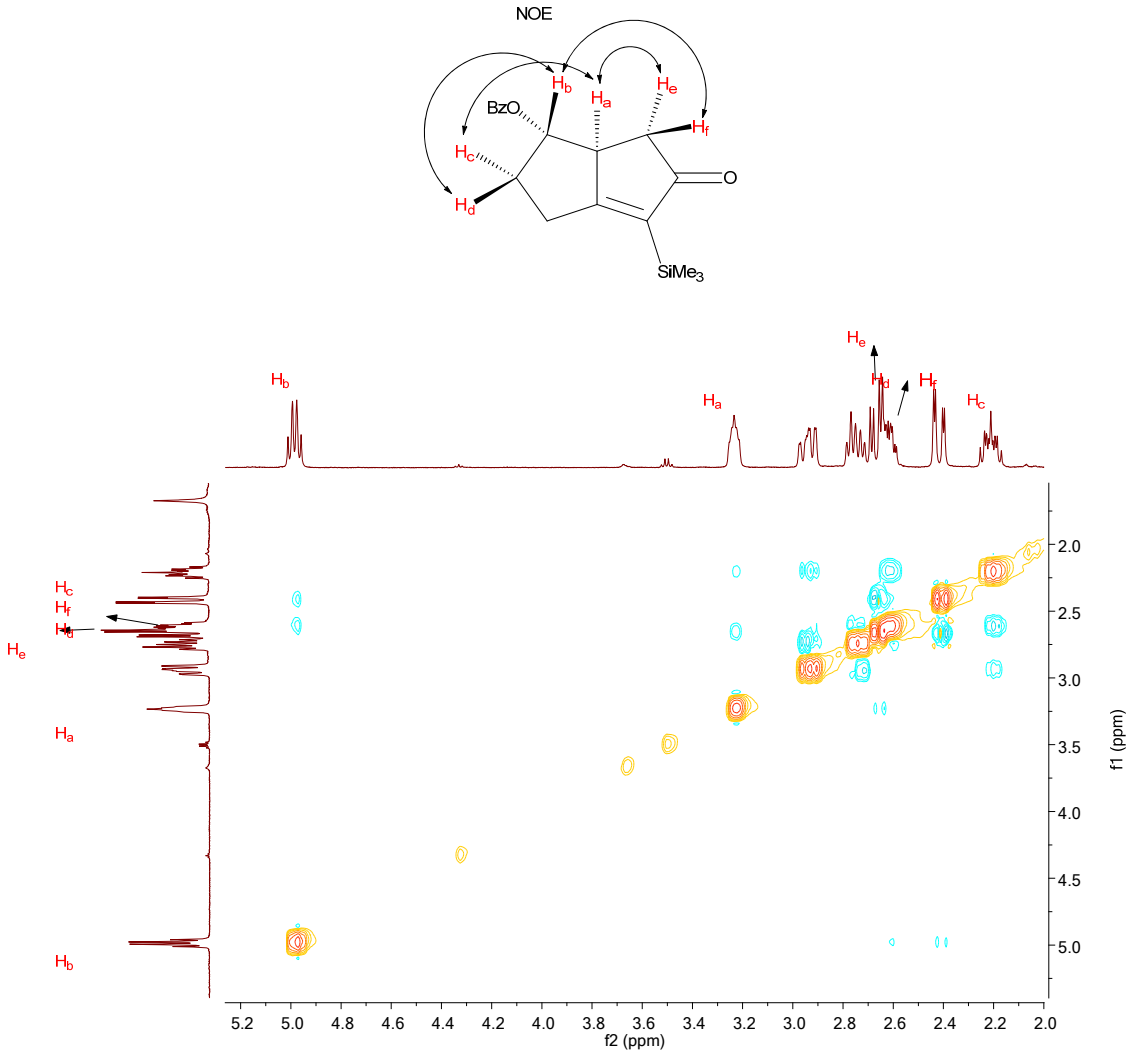
(1*S*,6a*S*)-5-Oxo-4-(trimethylsilyl)-1,2,3,5,6,6a-hexahydropentalen-1-yl benzoate (10a)

^{1}H-NMR



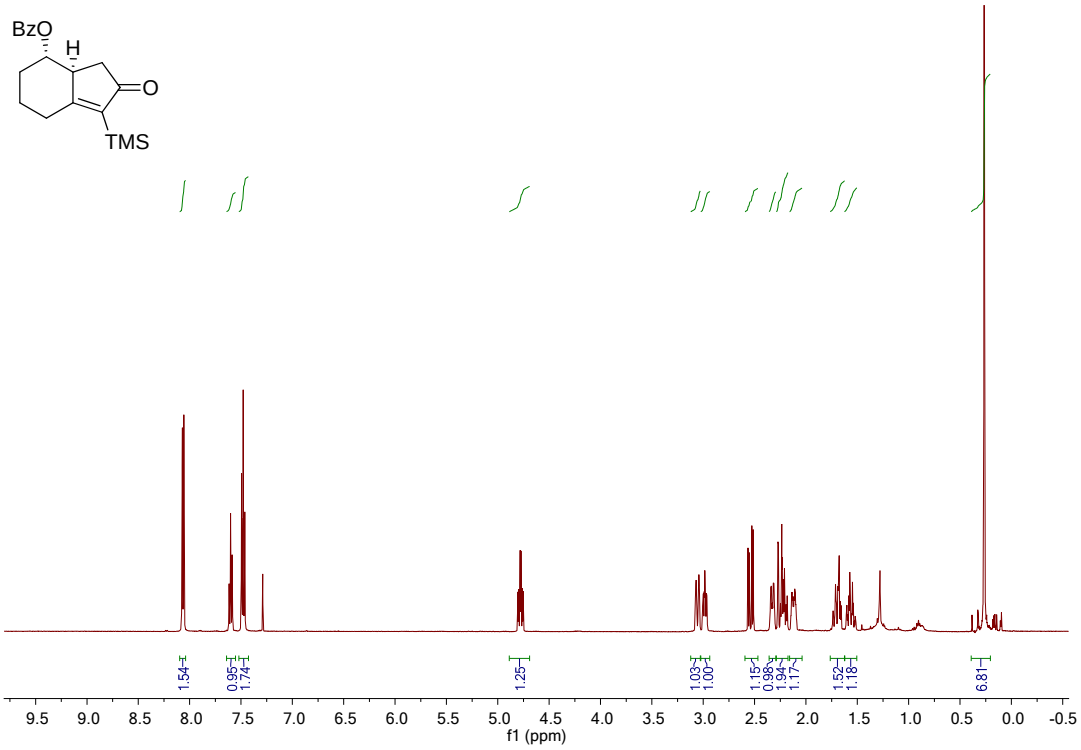
^{13}C-NMR



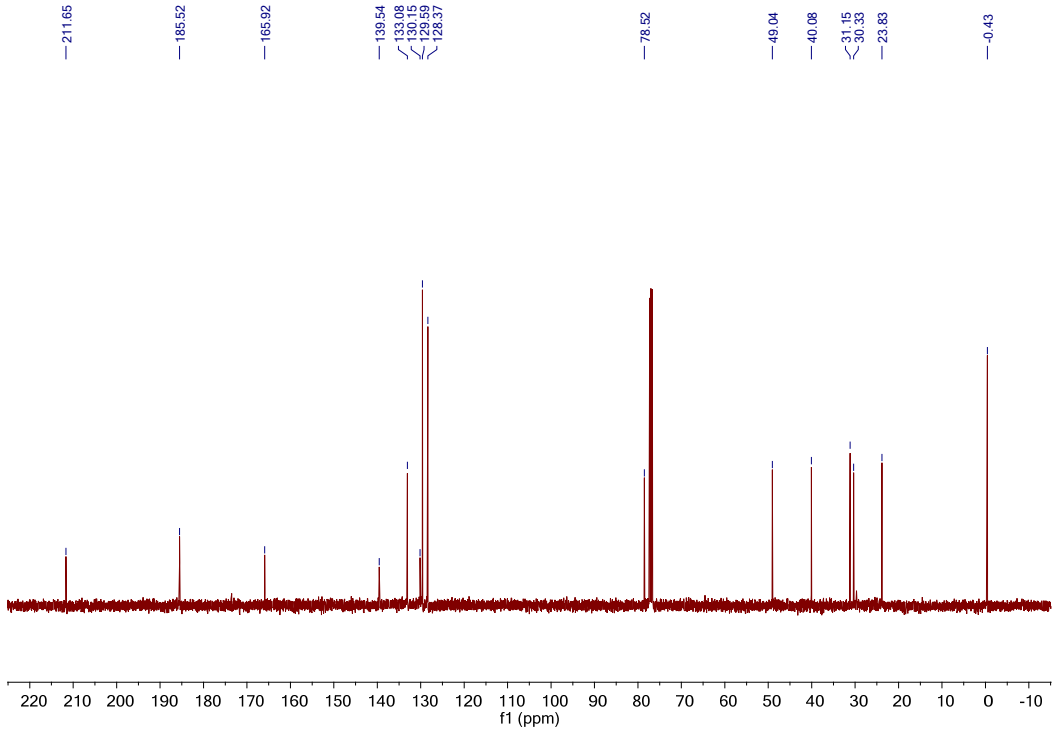

NOE
Hb
Ha
He
BzO
Hf
Hc
O
Hd
SiMe3
Hb
Ha
He
Hd
Hf
Hc
Hc
Hf
Hd
He
Ha
Hb
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
f2 (ppm)
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

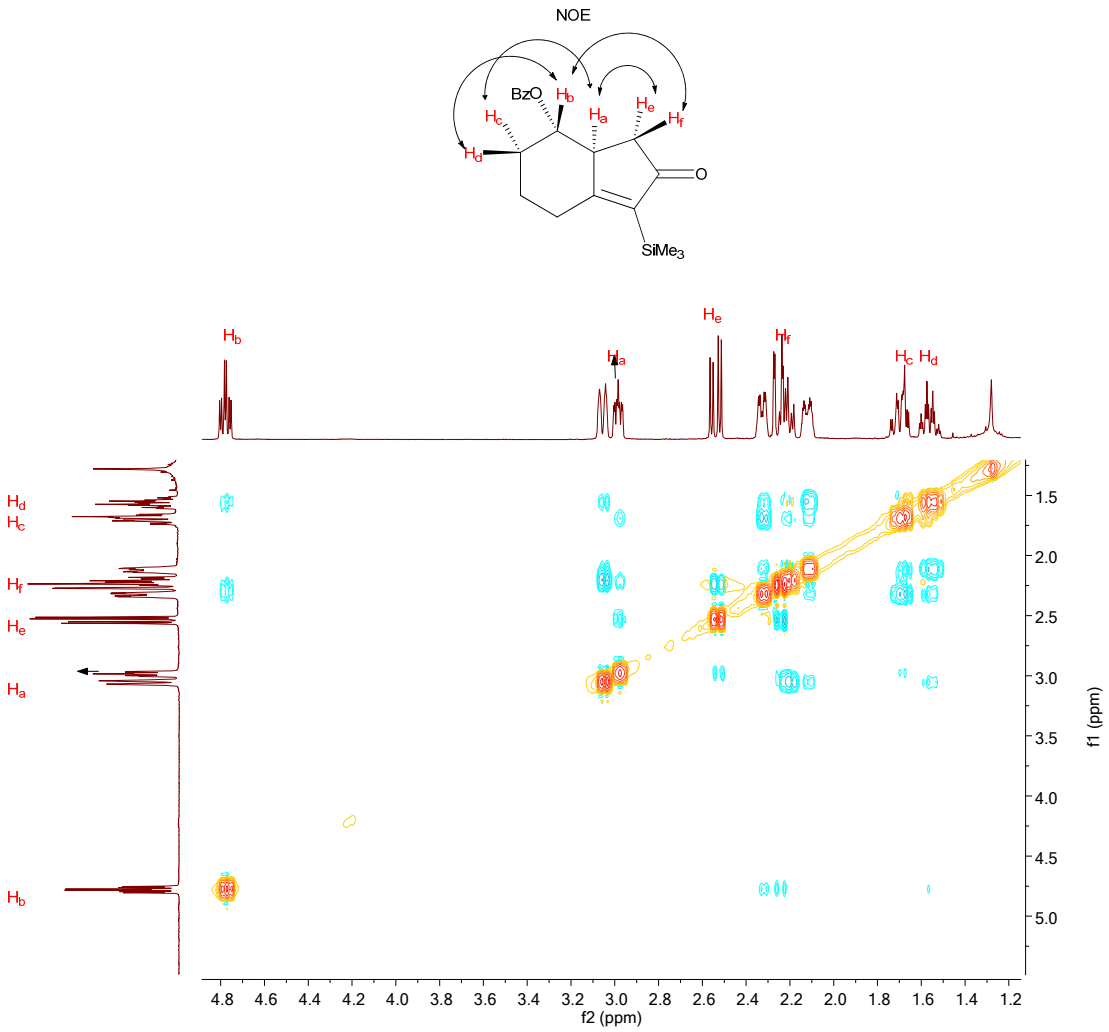
(7*S*,7a*S*)-2-Oxo-3-(trimethylsilyl)-2,4,5,6,7,7a-hexahydro-1H-inden-7-yl benzoate (10b)

^{1}H-NMR



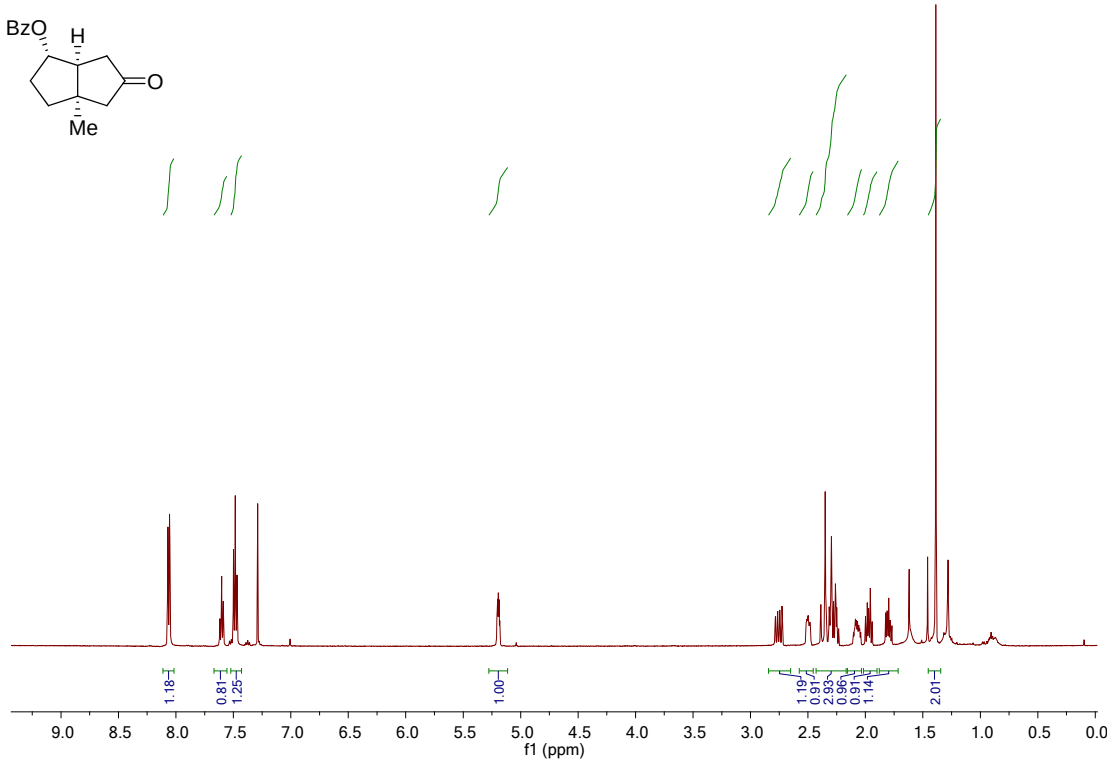
^{13}C-NMR



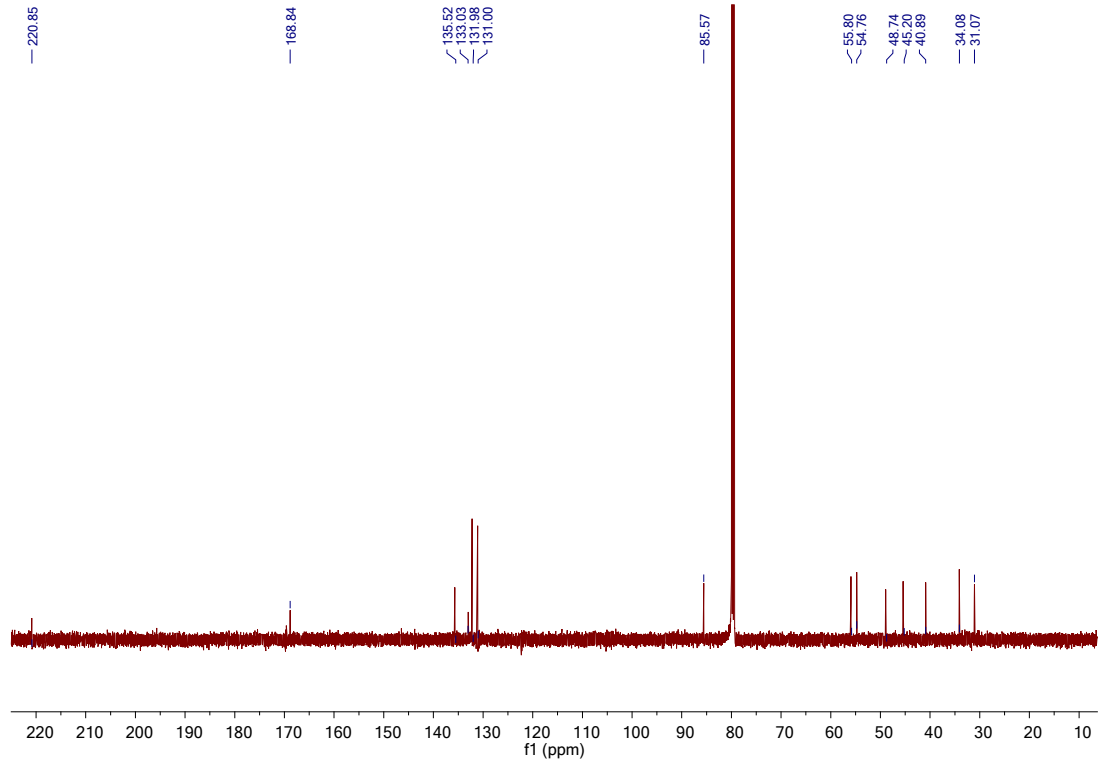

NOE
BzO
Hb
Ha
He
Hf
Hc
Hd
O
SiMe3
Hb
Ha
He
Hf
Hc Hd
Hd
Hc
Hf
He
Ha
Hb
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)
4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f2 (ppm)

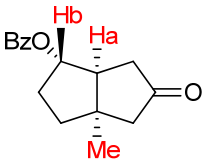
(1*S*,3a*R*,6a*S*)-3a-Methyl-5-oxooctahydropentalen-1-yl benzoate (11)

^{1}H-NMR

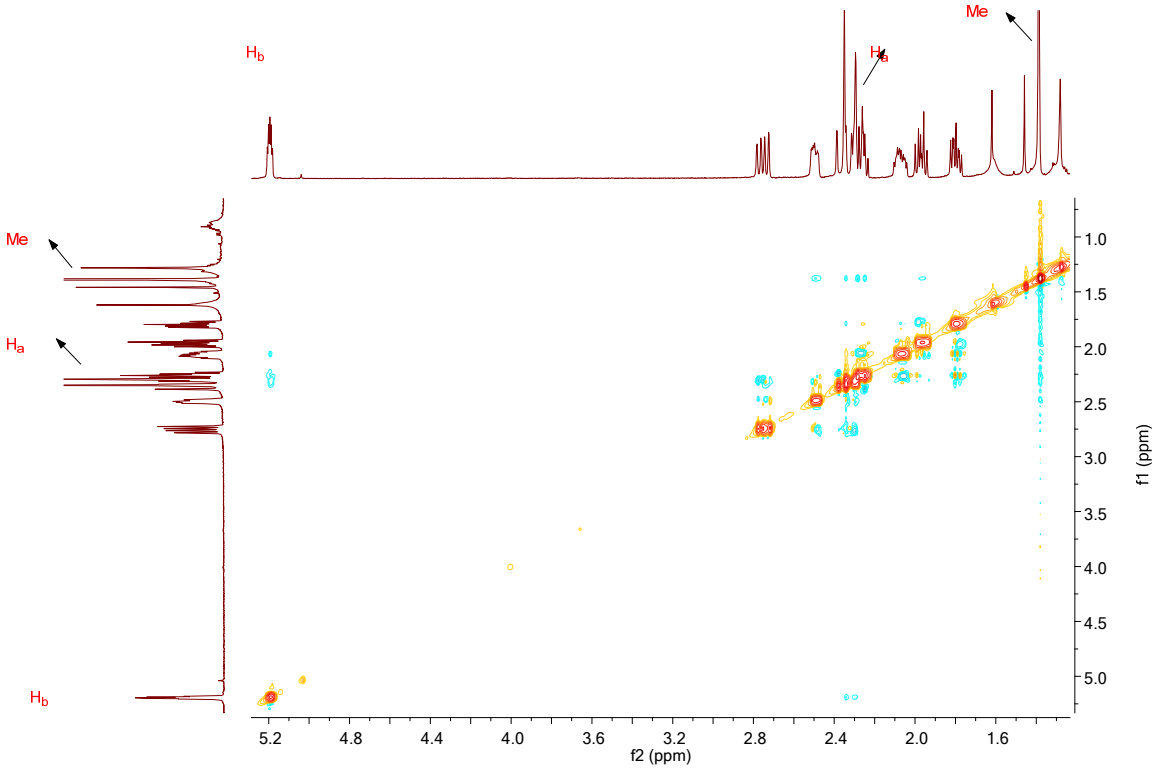


^{13}C-NMR



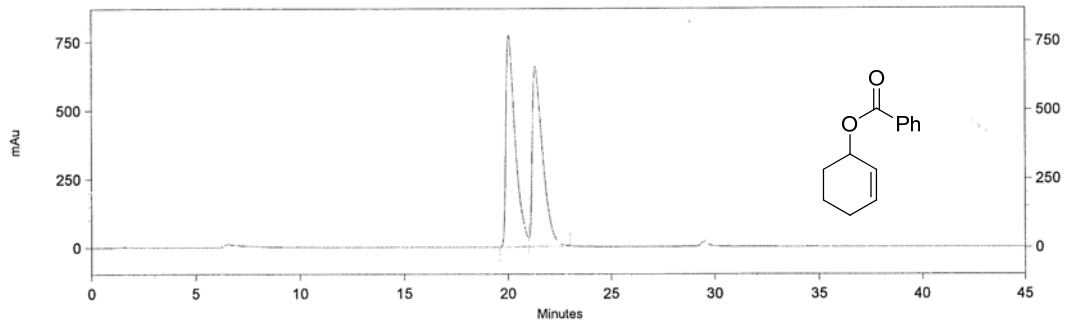


NOE between Ha and Me
No NOE between Hb and Me



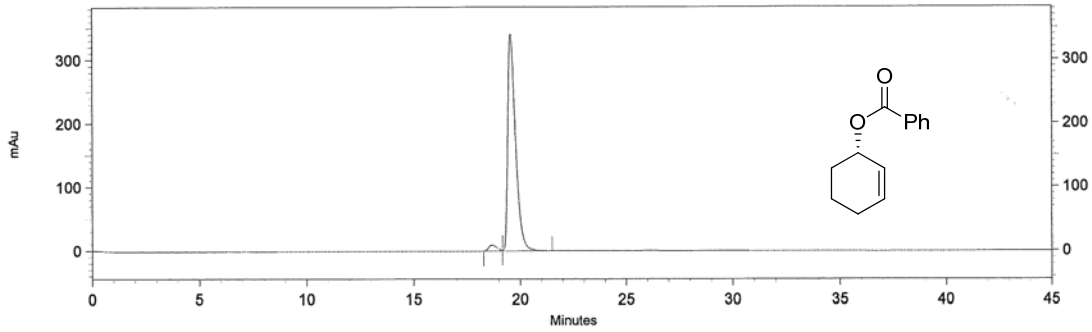
5. Representive HPLC Data

Compound 4b



1: 225 nm,
2 nm Results

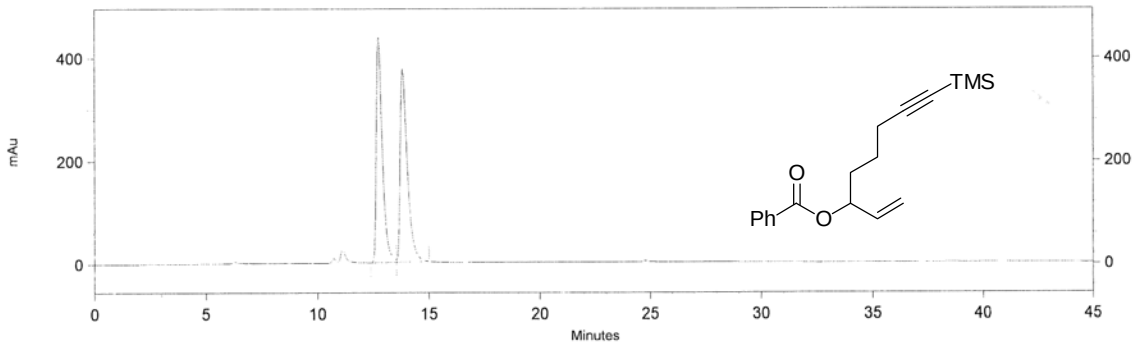
Pk #	Name	Retention Time	Area	Area Percent
1	1	20,032	24122656	51,338
2	2	21,312	22865274	48,662
Totals			46987930	100,000



1: 226 nm,
2 nm Results

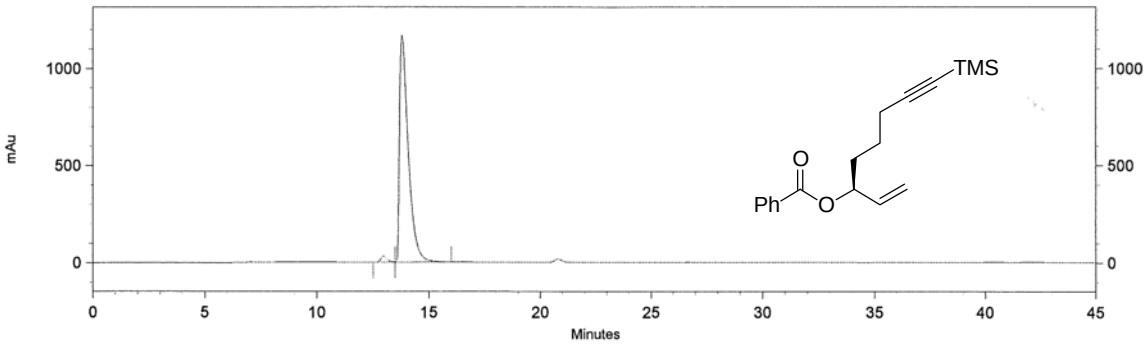
Pk #	Name	Retention Time	Area	Area Percent
1	1	18,660	250738	2,803
2	2	19,548	8695948	97,197
Totals			8946686	100,000

Compound 6b



1: 223 nm,
2 nm Results

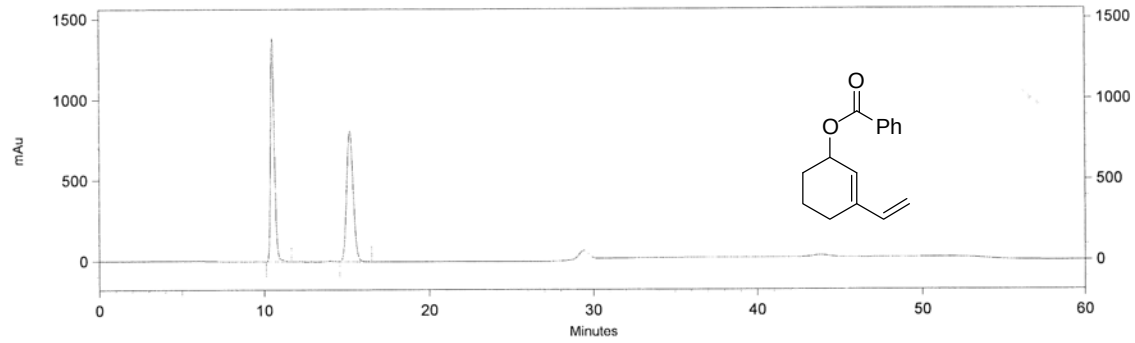
Pk #	Name	Retention Time	Area	Area Percent
1	1	12,740	8315523	49,827
2	2	13,820	8373245	50,173
Totals			16688768	100,000



1: 225 nm,
2 nm Results

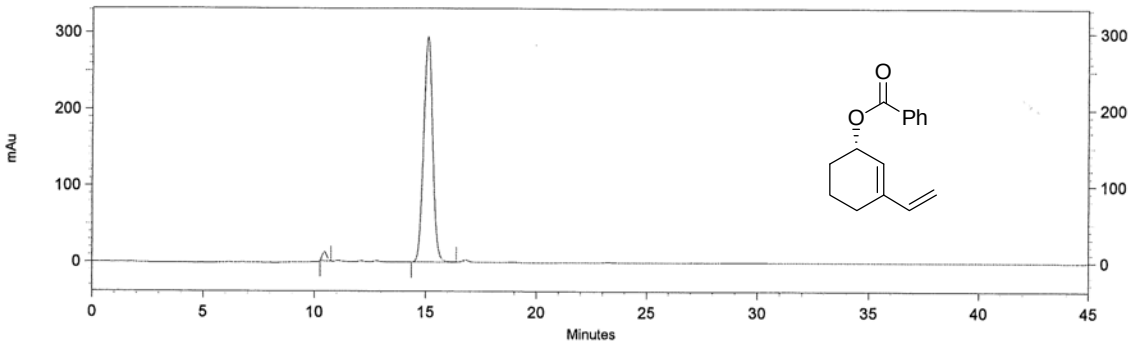
Pk #	Name	Retention Time	Area	Area Percent
1	1	12,976	577056	1,783
2	2	13,800	31778554	98,217
Totals			32355610	100,000

Compound 8b



1: 228
nm, 4 nm
Results

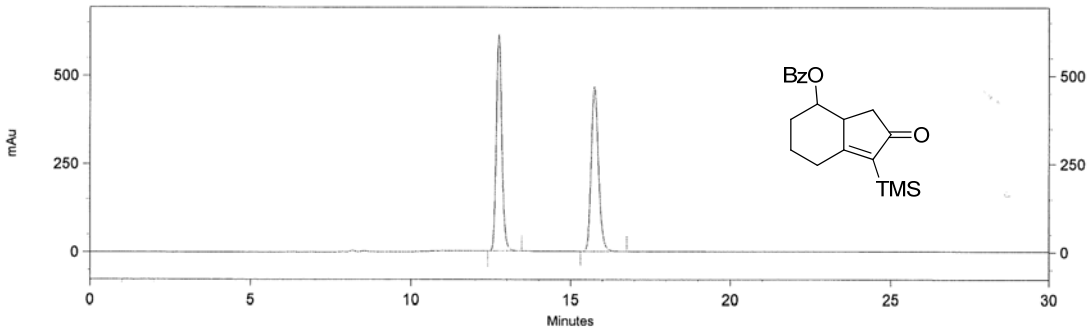
Pk #	Name	Retention Time	Area	Area Percent
1	1	10,504	22631459	50,205
2	2	15,188	22446917	49,795
Totals			45078376	100,000



1: 230 nm,
2 nm Results

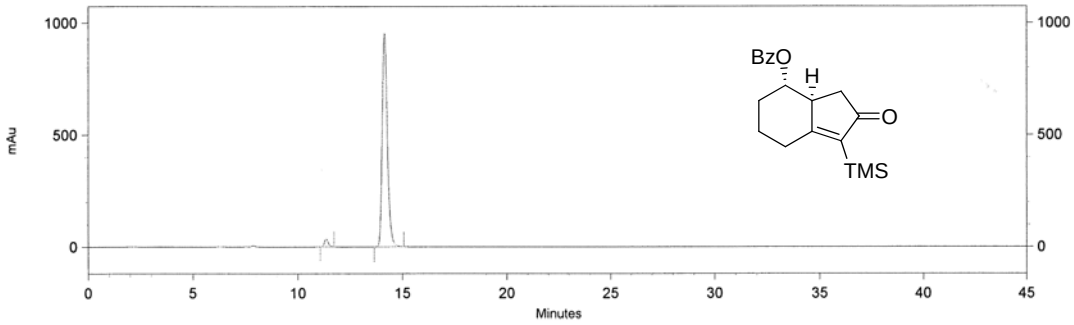
Pk #	Name	Retention Time	Area	Area Percent
1	1	10,448	165618	1,951
2	2	15,080	8323015	98,049
Totals			8488633	100,000

Compound 10b



1: 235 nm,
2 nm Results

Pk #	Name	Retention Time	Area	Area Percent
1	1	12,740	7468301	49,835
2	2	15,752	7517864	50,165
Totals			14986165	100,000



1: 230
nm, 2 nm
Results

Pk #	Name	Retention Time	Area	Area Percent
1	1	11,348	451480	2,665
2	2	14,140	16492492	97,335
Totals			16943972	100,000